THIN FILM HYDROGEN SENSORS:
A MATERIALS PROCESSING APPROACH

A Thesis in
Engineering Science and Mechanics

by
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Abstract

Hydrogen (H\textsubscript{2}) is consumed and produced in large quantities by chemical, petroleum, plastic, space and glass industries. Detection and quantitative estimation of H\textsubscript{2} in a reliable and efficient manner is of great value in these applications, not only from a safety standpoint but also economically beneficial. Hence the requirement for a simple but efficient hydrogen sensor.

The simplest hydrogen sensors are based on monitoring changes in electrical properties of group VIII transition metals, especially palladium (Pd). Hydrogen adsorbs on Pd surface and diffuses into its bulk altering its electrical and optical properties. This variation is used to detect/estimate hydrogen in the ambiance. However, at high hydrogen concentrations palladium undergoes a phase change. This causes an expansion of the lattice – a problem for fabricating reliable sensors using this metal. This problem was overcome by alloying palladium with nickel. Currently, sensors made from palladium alloy thin films (resistors and FET’s) can detect/estimate hydrogen from ppm to 100% concentrations. However, these sensors are affected by the total gas pressure and other gases like carbon monoxide (CO), sulfur dioxide (SO\textsubscript{2}), hydrogen sulfide (H\textsubscript{2}S). This work, for most part deals with resistors (chemiresistors). Resistors estimate hydrogen by correlating the change in resistance to the hydrogen concentration.

Magnetron sputtering enables the deposition of films of different compositions and morphology. In this work, Pd and Pd/Ni alloy thin films resistors were fabricated by sputtering. Morphology was seen to have a significant effect on the hydrogen sensing property of these films. In the presence of CO, the response of these sensors are extremely sluggish, however by employing SiO\textsubscript{2} barrier layer the response was greatly improved. It was noted that despite the sluggish response, the signal from the chemiresistors did saturate to same level as seen in absence of CO from gas mixture, contrary to the earlier results. Also, the geometry of the resistors did not have any effect on the sensor sensitivity or response.

Mass spectroscopy and ion energy distribution function (IEDF) analysis are important tools for characterizing processing plasmas. In this work, the sputter discharges were studied using energy and quadrupole mass spectrometer from Hiden. The IEDF of pulsed DC sputter discharges indicated a higher energy peak (∼65 eV) and a broad distribution in addition to the low energy peak (∼5 eV). The high energy peak was absent from the DC sputter discharge. This high energy peak was correlated to the pulsing of the DC source and was found to be independent of the target material.
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Chapter 1

Introduction

Inexpensive energy has been one of the driving force behind mankind’s technological development. During the course of history, mankind has moved from wood to coal, oil and natural gas (fossil fuels) as the fuel of choice. With increasing demand on these conventional fuels resulting in supply problems and environmental concern, there is a renewed interest in other fuel sources. Hydrogen has long been viewed as the fuel of the future. It is by far the most abundant element in the universe (∼90%), in fact it is the third most abundant element on earth (mostly in form of water). It burns cleanly in air (water being the product) and is non-toxic. It is also a possible source for nuclear fusion. However, lingering doubts about its safety, difficulty in storage and handling has prevented fulfilling its potential and replacing the current petroleum based economy with a hydrogen based economy. Vital to this transformation is the development of efficient detection and sensing technology.

1.1 Detecting/Sensing Hydrogen – Why is it necessary?

The infamous Hindenburg (Zeppelin airship) crash in 1937 lent credence to the notion of hydrogen being an extremely dangerous gas. However, it is far less dangerous when compared to the all popular fuel - gasoline. Hydrogen has a much higher self-ignition temperature (510°C) than gasoline (228 – 501°C depending on the grade) [1]. Moreover, being the lightest element, it disperses rather rapidly in atmosphere as opposed to heavy gasoline vapor, which lingers on the surface. However, its low mass and high diffusivity makes it difficult to store. Also, it is highly flammable in concentrations ranging from 4% to ∼90% by volume [1]. Hence there is an absolute need for efficient hydrogen detectors/sensors.
A multitude of industries use H₂ either as part of their process or as a fuel. Some of the major industries are

- Chemical industries – refining crude oil, plastics, reducing environment in float glass industry, etc
- Food industry – hydrogenation of oils and fats
- Semiconductor industry – as processing gas in thin film deposition and in annealing atmosphere.
- Transportation – as fuel in fuel cells, rockets for space vehicles

In addition to safety concerns, accurate and real-time estimation of H₂ in the process is of great economic value for these industries. For example, in a refinery, the exhaust of the refining process contains H₂ which is recycled and fed back to the process stream. It is of great economic benefit to the gas supplier to have a good estimate of the H₂ content in the exhaust in real time. APCI (Air Products & Chemicals Inc) estimates that it can save $95,000/annum/refinery by estimating H₂ content accurately in the exhaust in real time [2]. Likewise, a good hydrogen leak detector is vital for safe functioning of hydrogen powered vehicles.

1.2 Hydrogen Sensing Technologies

For the application discussed above, the desired characteristics of a good hydrogen sensor are – good sensitivity (respond to low concentrations of H₂), rapid response and inert with regard to chemical reactivity with the ambiance. In fact, an ideal chemical sensor could be thought to have the following characteristics

- Chemically selective i.e detect H₂ within any gas mixture.
- Reversible and rapid response.
- Highly sensitivity – leak detectors should be able to detect trace amounts of H₂.
- Insensitive to ambient temperature and pressure variations– responds to absolute fraction of H₂ only.
- Simple to operate, compact and cheap.
It is highly unlikely that any one sensor technology could satisfy all of the above mentioned criteria.

Currently, there are numerous H₂ sensor technologies [3], most of these technologies could be classified under the following categories

Mass spectroscopy
This works like a conventional mass spectrometer, scanning a gas sample for a specified range of masses starting from 1 amu (atomic mass unit). This is a very selective technique i.e it can detect hydrogen in a gas mixture. However its response time is somewhat long in that each scan cycle take around ten to fifteen minutes. More importantly, mass spectroscopy needs elaborate gas handling system to extract a gas sample to analyze. This makes it expensive and bulky, hence useful only in limited applications.

Gas chromatography (GC)
This system extracts H₂ gas from a gas sample by passing it through a separation column and subsequently detecting it using a mass spectrometer. Like a mass spectrometer this is also a highly selective technique. However this method also suffers from the problems associated with a mass spectrometer.

Thin film sensors
This comprises of a wide variety of sensor technologies based on palladium (Pd) thin films. All the sensors detect H₂ by monitoring changes to mechanical, electrical or optical properties of Pd thin films. Unlike other technologies, these sensors are compact and have a fast response. However, they are susceptible to poisoning by other gases and hence not very selective.

1.2.1 Thin Film Hydrogen sensors

As described above, these sensors are largely based on palladium (Pd) thin films. Hydrogen tends to adsorb on Pd surface and subsequently diffuse into the bulk. The reaction could be written as

\[ \text{H}_2 \rightleftharpoons 2\text{H}_{\text{ad}} \]  (1.1)

\[ \text{H}_{\text{ad}} \rightleftharpoons \text{H}_{\text{Me}} \]  (1.2)
where, \( H_{ad} \) represents adsorbed hydrogen atoms on the Pd surface and \( H_{Me} \) represents dissolved hydrogen in Pd lattice. Incorporation of \( H_2 \) alters the electrical and mechanical properties of the film. This change is utilized in detecting and quantifying the amount of \( H_2 \) in the ambiance. Listed below are some of the sensor technologies that use Pd thin film as the active material to detect \( H_2 \) [3].

**Metal Oxide Semiconductor (MOS) devices**

In these devices (capacitors, field effect transistors - FET) the adsorbed hydrogen (on Pd) forms a dipole at the metal oxide interface. This causes a change in the electrical characteristics of the device.

**Resistors**

Change in resistivity of Pd in the presence of hydrogen is monitored to detect/estimate the \( H_2 \) content in the ambiance. These devices are also referred to as chemiresistors.

**Pyroelectric sensor**

In pyroelectric material the polarization is a function of temperature. Hence, variation in temperature causes a potential difference between opposing surfaces in this material. In this technology, a thin film of Pd is deposited on the surface of a pyroelectric material. When exposed to \( H_2 \) it adsorbs on the Pd surface. The heat of adsorption for this process produces a potential difference that is used to detect/estimate \( H_2 \).

**Piezoelectric sensors**

The oscillation frequency of a piezoelectric material is a function of its mass (mass of the crystal and any coating on it). Adsorption of \( H_2 \) on Pd coated piezoelectric material will alter its oscillation frequency. This alteration is used to detect \( H_2 \).

**SAW (Surface Acoustic Wave) sensors**

Adsorbed \( H_2 \) on a Pd thin film perturbs surface acoustic wave on a piezoelectric substrate. This property is utilized in this class of sensors.

**Fiber optic sensors**

These sensors are essentially optic fibers coated with Pd. The adsorption of \( H_2 \) on the Pd surface alters the optical property of the fiber (absorbance, reflectance, luminescence or scattering) [4].
1.3 Metal-Insulator-Semiconductor Device

MOS based hydrogen sensors were first reported by Lundström et al [5, 6]. These devices consist of a Pd metal gate deposited on a thermally grown gate oxide (see Figures 1.1, 1.2). In presence of H₂ the gas molecules adsorb on the metal surface and dissociate into hydrogen atoms that diffuse to the metal oxide interface. A dipole is formed at the interface (Figure 1.1) and this alters the effective electric field seen by the semiconductor surface. In a capacitor, the dipole formation alters the flat band voltage (the voltage at which there is no band bending in the semiconductor). In case of the FET, the dipole causes a shift in the threshold voltage due to change in the net field seen by the channel (region under the gate, between the source and drain, see Figure 1.2).

In case of Schottky diodes (Pd thin oxide semiconductor), adsorption of H₂ is thought to lower the effective work function of Pd modifying the electric characteristics of the device [8]. The presence of H₂ is indicated by an increase in the reverse current in the diode.

These sensors are extremely sensitive and can detect H₂ down to ppm range. However, they get saturated at around few tens of thousands of ppm of H₂. Hence these sensors are ideally suited for leak detection.
1.4 Chemiresistors – Wide Range Hydrogen Sensors

This is one of the simplest sensor structures. It consists of a thin Pd strip exposed to the ambient gases. When exposed to H\(_2\) the gas molecules adsorbs and dissociates on the surface. The adsorbed hydrogen atom diffuses into the thin film and occupies the interstitial lattice sites (see Figure 1.3). This results in increased scattering of electrons causing an increase in the resistivity of the film. The change in resistivity is directly related to the amount of H\(_2\) present in the metal film which in turn is related to the amount of H\(_2\) in the ambience.

These sensors can theoretically detect H\(_2\) from around 0.5% to 100% by volume. However, Pd undergoes a phase change (from hydrogen deficient \(\alpha\) phase to hydrogen rich \(\beta\) phase) for concentration of hydrogen in excess of \(\sim\)10 atomic % at room temperature and atmo-
spheric pressure. This change is accompanied by an increase in the lattice volume causing mechanical instability in the metal film.

1.4.1 Better Chemiresistors – Challenges and Solutions

To fulfill the potential of a chemiresistor as a wide range H\textsubscript{2} sensors capable of detecting H\textsubscript{2} up to 100% by volume, the single phase region in the metal-hydrogen phase diagram has to be extended. Alloying Pd with other metals like iron, silver, copper, nickel would enhance the single phase region. Hughes and his co-workers [9] demonstrated that by alloying Pd with Ni (≥8 atomic %) they could prevent the phase transformation from occurring. However, these films are less sensitive to H\textsubscript{2} than pure Pd films.

Another issue plaguing Pd thin film sensors are their ineffectiveness at detecting H\textsubscript{2} in gas mixtures, for example, gas mixtures containing H\textsubscript{2} and carbon monoxide (CO). CO competes with H\textsubscript{2} for adsorption sites on Pd surface preventing H\textsubscript{2} from adsorbing on the surface. This delays the response of the sensor. In this work, selectively permeable barrier layers are used to avoid this problem. These layers preferentially allow H\textsubscript{2} molecules to diffuse through while preventing other gas molecules from doing so. In microelectronics, SiO\textsubscript{2} has long been known to be permeable to H\textsubscript{2}, hence, high quality sputter deposited SiO\textsubscript{2} films have been used to improve the performance of chemiresistors in complex gas mixtures containing CO and other gas molecules that poison the Pd metal surface.

As described before, the key steps in the working of thin film sensors is the adsorption of H\textsubscript{2} molecule on the Pd surface. Hence, the surface morphology would be an important parameter in the performance of these sensors. Magnetron sputter deposition enables us to alter the morphology by controlling the deposition parameters like input power (DC or pulsed DC), ion bombardment and deposition pressure. In this work, the effect of morphology of the Pd films on the sensor performance has been investigated.
References


Chapter 2

Literature Survey

Interaction of hydrogen ions and molecules/atoms with solid surfaces and bulk is crucial in material science (hydrogen embrittlement in metals), chemical reactions (catalysis) and in microelectronics (reliability of semiconductor devices [1]).

2.1 Metal-Hydrogen Interaction

Interaction of gaseous hydrogen with metals, in most cases, are governed by four processes, namely, adsorption of molecular H$_2$ on the metal surface, dissociation of the molecule leading to formation of H atoms, migration of H atoms into the bulk of the metal and possibly reaction between H and metal atoms leading to formation of a hydride [2]. The first process - adsorption is often the rate limiting step in the overall reaction. On many metal surfaces, H$_2$ does not dissociate and diffuse into the bulk, but sticks to the surface (physisorption). The molecule is held to the surface by van der Waals force. The binding energy for this process is rather low (∼10 - 20 kJ/mol). Adsorption of H$_2$ on Al, Au and Ag at low temperature falls into this category. On the other hand, chemisorption on the metal surface leads to dissociation and subsequent diffusion of hydrogen atom into the bulk, as is the case with H$_2$ on transition metals like Pd, Ni and Pt. The dissociation is attributed to interaction of sp or d wavefunction of the metal atom with the 1s wave function of the hydrogen atom. The energy associated with the interaction is sufficient to break H-H bond. Binding energy associated with chemisorption is ∼80 - 120 kJ/mol. In these metals the d-band maxima is close to the Fermi level unlike the noble metals such as Au where the d-band is around 2 to 3 eV below the Fermi level [2]. After dissociation, the H atom diffuses into the metal and
occupies interstitial sites. In metals with fcc (face centered cubic) lattice, hydrogen atoms usually occupy the octahedral interstitial sites while in metals with a bcc (body centered cubic) lattice, they usually occupy the tetrahedral sites. As a rule, if the hydrogen is more electropositive than the metal, it tends to loose electrons to the conduction band of the metal and hence would tend to seek sites with higher electron density, which, in the case of fcc lattices happens to be the octahedral sites [3]. However, if hydrogen is less electropositive, then it would go to tetrahedral sites as is the case in bcc lattice. Hydrogen, the smallest atom, diffuses rapidly in the metal lattice, jumping between the interstitial sites. At low temperatures (<50 K) the diffusion process is thought to occur by tunnelling through the barrier between the interstitial sites. However, at higher temperature hydrogen atoms have sufficient energy to jump over the potential barrier separating the interstitial sites.

2.2 Palladium-Hydrogen System

Palladium was discovered in 1803 by Wollaston while working on purification of platinum. The element was named after Pallas the Greek goddess of wisdom [4,5]. It belongs to group VIII transition elements, also referred to as “platinum metals”. It has a fcc crystal lattice. The primary sources of Pd are copper-nickel sulfide ores and crude platinum. Thomas Graham, a British chemist, discovered in 1866 that Pd metal could absorb large quantities of H\textsubscript{2} [4]. He also observed that H\textsubscript{2} could diffuse through Pd membranes at a rapid rate and, hence, be used to purify H\textsubscript{2} [4,5]. The measured diffusivity of hydrogen in Pd indicates that it is orders of magnitude larger than diffusivities of other gases. Also, the surface of Pd is considered to be highly permeable to H\textsubscript{2}. Based on the available data, Völk and Alefeld [3, 5] calculated an expression consistent with the Arrhenius law for diffusivity of hydrogen in Pd

\[ D = D_0 \exp\left(-\frac{E}{k_B T}\right) \]  

(2.1)

where the activation energy \( E = 0.23 \) eV and the diffusion coefficient of hydrogen in Pd \( D_0 = 2.9 \times 10^{-3}\) cm\(^2\)/s. Figure 2.1 shows the diffusivity of hydrogen in Pd calculated from equation 2.1 for temperatures between 200 and 1000 K.

Pd-H is one of the most well studied metal-hydride systems. In bulk Pd, H atom occupies octahedral interstitial sites in the fcc lattice. As is characteristic of such systems, Pd-H is a two phase system with \( \alpha \) (low hydrogen concentration – H/Pd \( \leq 0.025 \) to 0.03 at. % at \( \sim 298 \) K) and \( \beta \) (high hydrogen concentration – H/Pd \( \geq 0.6 \) at. % at \( \sim 298 \) K) phases
(0.03 ≤ H/PD ≤ 0.6 – two phase α+β region) [5]. At low hydrogen concentrations, some of the octahedral sites are occupied (see Figure 2.2). At higher concentrations of hydrogen most of the octahedral sites are occupied, giving rise to the β phase. When all the octahedral sites are occupied, the Pd-H lattice resembles the NaCl structure (two interpenetrating fcc lattices). Figure 2.2 shows the change in H atom occupation of interstitial site in <110> plane in Pd lattice. Increased concentration of H in Pd causes a doubling of the occupied...
sites as PdH undergoes a phase transformation. This phase transformation is accompanied by an expansion of the lattice. However, PdH retains the fcc lattice.

\[ a(0) = 3.890\text{Å}, \quad a(\alpha_{\text{max}}) = 3.894\text{Å}, \quad a(\beta_{\text{min}}) = 4.025\text{Å} \]

The increase in the lattice volume resulting from the $\alpha \rightarrow \beta$ is about $\Delta V = 1.53 \text{ cm}^3/\text{g-atom}$ of H. This change in lattice volume is responsible for mechanical instability of Pd films in ambients with high hydrogen concentration. The formation of PdH is attributed to filling of the d band in Pd by electrons (one electron per H atom) donated by H atoms (rigid band model). However, data on the band structure of Pd indicates that there are very few vacant sites in the d band in Pd. This has given rise to other models that suggest s-p band interactions as well.

### 2.2.1 Mechanism of H$_2$ absorption in Pd

Hydrogen permeates into Pd in a two step process. The first step consists of absorption of hydrogen on the metal surface and its dissociation into atomic hydrogen ($H_{ad}$). H$_2$ adsorbs preferentially on the three fold and four fold “hollow” sites (fcc and bcc). The dissociation of H$_2$ on the surface leads to occupation of two sites, hence for adsorption of one H$_2$ molecule

![Figure 2.3: Phase diagram of Pd–H system [4]](image)
there should be at least two available sites on the Pd surface. Subsequently, atomic hydrogen diffuses into the bulk, occupying the octahedral interstitial sites of the Pd lattice (fcc). The two step process could be represented as follows:

\[
\begin{align*}
    
    \text{H}_2 & \iff 2\text{H}_{\text{ad}} \\
    \text{H}_{\text{ad}} & \iff \text{H}_{\text{Me}}
\end{align*}
\]

(2.2)  
(2.3)

If step 1 is considered to be the rate determining step, then the rate of hydrogenation is proportional to the partial pressure of hydrogen \(p_{\text{H}_2}\) while the rate of dehydrogenation would be proportional to the square of the lattice concentration of hydrogen, \(n^2\). However, if step 2 is the rate determining step then the rate of hydrogenation would be proportional to \(\sqrt{p_{\text{H}_2}}\) and rate of dehydrogenation would be proportional to concentration of hydrogen in the lattice. Measurements carried out between 20°C and 150°C for low hydrogen concentrations (\(\alpha\) phase) lead to the following rate law (equation 2.4) [8]

\[
\frac{dn}{dt} = kP_{\text{H}_2}(1 - \theta) - k'n^2\theta
\]

(2.4)

where 
\(\theta = \text{fraction of occupied surface sites}\)
\(n = \text{concentration of hydrogen in the lattice}\)
\(k = \text{rate constant for dissociation of H}_2\)
\(k' = \text{rate constant for recombination of adsorbed hydrogen (H}_{\text{ad}})\)

Since the resistance of the metal hydride is proportional to the hydrogen content in the metal, the above equation yields directly the relation between resistance change and hydrogen concentration shown in Figure 2.4. The linear regions at the onset of hydrogenation and dehydrogenation represent purely diffusion limited response of the palladium film. The deviation from linearity indicates that other mechanisms dictate change in resistance of the film. In this case, the response is governed by the reactions 2.3.

The thermodynamics of dissociation and subsequent dissolution of hydrogen in Pd is governed by Langmuir-type isotherm. In a Langmuir isotherm, the fraction of occupied surface sites \((\theta)\) is proportional to the partial pressure \((P)\) of the gas, however, for a diatomic gas that dissociates on the metal surface upon adsorption, as is the case in \(\text{H}_2\), \(\theta\) is proportional to \(\sqrt{P}\) for low concentrations of gas, as given by Seivert’s law. For adsorption of \(\text{H}_2\) on Pd,
Seivert’s law could be expressed as follows:

\[
\ln \sqrt{P_{H_2}} = \ln \left( K \frac{n}{1 - n} \right) \quad (2.5)
\]

\[
n = \frac{H}{P_{Pd}} \quad (2.6)
\]

\[
K = \exp \left[ \frac{\Delta H^\circ}{2RT} + \frac{\Delta S^\circ}{2R} \right] \quad (2.7)
\]

where \( P_{H_2} \) is the partial pressure of \( H_2 \), \( \Delta H \) is the enthalpy of adsorption, \( \Delta S \) is the entropy of adsorption, \( R \) is the gas constant and \( T \) is the temperature.

### 2.3 Palladium Chemiresistors – Working and Mechanisms

Change in resistivity is one of the many observed changes in physical properties of Pd on adsorbing \( H_2 \). The change is attributed to increased scattering of electron by H atoms occupying the interstitial sites. The rate of resistance change follows the rate of hydrogen dissolution into Pd. Data in the literature for change in resistivity of Pd in presence of \( H_2 \), indicates two linear regimes correspond to the \( \alpha \) and \( \beta \) phase \[4\]. The maximum change in resistance \( (dR/R) \) observed at room temperature for the \( \alpha \) phase is about 8% for \( \sim 3 \) atomic % H in Pd. Chemiresistors can detect concentrations in excess of 0.5 % \( H_2 \) at atmospheric pressure.
2.3.1 Palladium/Nickel Alloy Chemiresistors

Nickel forms a binary substitutional alloy with Pd. It is completely miscible in Pd and has a single phase for the entire range of compositions (0 to 100% Ni). Being a smaller atom (atomic radius of Ni = 1.62 Å and atomic radius of Pd = 1.79 Å [9])¹, alloying of Pd with Ni contracts the lattice. The lattice constant of Pd-Ni alloys has nearly linear dependence as a function of Ni content (in atomic %). The lattice parameter decreases as the Ni content increases, from 3.89 Å for Pd to 3.52 Å for Ni [4]. Data on solubility of hydrogen in Pd/Ni alloys at 760 torr and 25°C indicates that there is a sharp drop in solubility as Ni content increases from 10 to 20 atomic % [4]. This results in reduced sensitivity of these alloy films to H₂. For alloys with Ni content in excess of 25 atomic %, there is negligible solubility. The contraction of the lattice is thought to be responsible for lower hydrogen solubility at room temperature and pressure, hence for preventing a phase change in the alloy thin films.

The electrical resistivity of the alloy changes with the composition of the alloy, following a curve with a flattened peak at around 30 atomic % Ni (Figure 2.5). The peak would correspond to maximum distortion of the lattice as a result of alloying. Pd/Ni alloys with Ni content in excess of ~8 atomic % exhibit smaller changes in resistivity when exposed to H₂ [4]. This is consistent with the lowered solubility of H in Pd/Ni alloys.

![Figure 2.5: Bulk resistivity change in Pd-Ni alloys as a function of alloy composition at 300 K [10](image)](image)

Hughes et al [11,12] demonstrated that Pd/Ni alloy thin films with Ni content in excess of 8% did not show phase change for all concentrations of H₂ at 700 torr pressure. They were

¹see www.webelements.com
successful in fabricating chemiresistor structures with Ni content in the range of 8 to 15%, that had good sensitivity to H$_2$. Their work also indicated that these alloy films showed small deviation from Sievert’s law. This deviation was related to the alloy composition. These devices were fabricated by depositing alloy films by electron-beam evaporation and, hence, had limited control over thin film morphology. However, chemiresistors tested after being subjected to different annealing treatments that resulted in different morphology indicate that coarser grained films had lower sensitivity to H$_2$ when compared to finer grained films [13]. The annealing step (at temperatures above 350°C in forming gas - 4% H$_2$ in Ar) also improved the stability of the sensor performance by eliminating drift.

2.3.2 Effect of Competing Gases

Apart from H$_2$, gases like CO, O$_2$, H$_2$S, SO$_2$, NO$_2$ adsorb on metal surfaces. CO and H$_2$S readily adsorb on Pd and compete with adsorption of H$_2$. CO molecules compete with H$_2$ molecules in occupying the available sites on the metal surface, however, unlike H$_2$, CO does not diffuse into the metal. Hence, it blocks adsorption sites for H$_2$ and potential pathways for release of hydrogen from the metal surface to the ambient. This leads to sluggish response and drift in resistor performance. Sulfur containing gases also poison the catalyst in a similar manner, however the change is irreversible.

CO physically adsorbs on Pd and has an initial sticking coefficient$^2$ of $\sim$1 at room temperature [14, 15]. This is in contrast to H$_2$ which has a sticking coefficient on Pd close to 0.6 to 0.7 at room temperature. Thus, CO would adsorb preferentially on Pd (Figure 2.6). CO tends to occupy the top, bridge or the hollow sites$^3$ (fcc and bcc). Energetically all these

![Figure 2.6: Schematic of adsorption of CO on Pd chemiresistor.](image)

$^2$ratio of number of adsorbed molecules on the surface to the number of molecules impinging on the surface

$^3$site between three or four atoms in contact with each other
sites are considered to similar, however, CO tends to start adsorbing on the hollow sites. At higher surface coverage, it starts to occupy the bridge and finally the top sites [14,16–19]. Measurements (LEEDS, STM, etc) on single crystal Pd surfaces indicate that CO tends to form ordered clusters, occupying certain preferred sites [18,19]. Hydrogen permeation experiments performed by Amano et al [20] on Pd in presence of CO at temperatures ranging from 150°C to 400°C indicate that the permeability of H₂ drops significantly at temperatures below 200°C in presence of 10 to 50% CO. There was little difference in the permeation of H₂ for different concentrations of CO in this range. Experiments performed on single crystal Pd also indicate that defects on the surface act as additional sites for adsorption of CO [18].

Measurements made on MIS devices (MOS capacitors, MOSFETS, Schottky diodes) with Pd gate indicate that CO adsorption influences H₂ sensing capabilities of these devices. Lundström et al show that there is a slowing down of the response of MOS sensors to H₂ in presence of CO [21–23]. Occupation of surface sites by CO is attributed to the sluggish response. However, at small concentrations of CO there is little effect on the sensitivity to H₂ [22,24]. At higher concentrations (>2%), CO tends to attenuate and slows the response of MIS sensors. This is attributed to blocking of the surface sites thereby preventing adsorption of H₂. In chemiresistors (Pd/Ni alloys), CO (>2%) slows the sensor response to H₂ significantly [25].

O₂ is thought to react on the Pd surface in presence of H₂ and, hence, affect Pd thin film sensors. Like H₂, O₂ dissociates on the surface of Pd and occupies surface sites. In presence of H₂, it reacts with H to form H₂O. This reaction has been observed to occur on MIS devices (with Pd gate) at elevated temperature (~473 K) [21]. STM and AFM studies on Pd thin films indicate surface changes in the film as a result of exposure to O₂ and H₂ at elevated temperatures and atmospheric pressure, suggesting that O₂ adsorbs on the surface and interacts with H₂ on the surface [26]. At room temperature, the effect of O₂ is reported to be small [24,27].

Sulphur containing gases, like H₂S and SO₂, poison Pd by forming sulphur deposits on its surface [28]. H₂S adsorbs and dissociates on the surface forming atomic H and S. Hydrogen atoms diffuse into the bulk, while sulphur atoms are left behind on the surface, permanently blocking other surface sites. Similar effect is also seen with SO₂, although to a far lesser extent. The poisoning of Pd by these gases is irreversible. As a result, Pd based hydrogen sensors lose sensitivity to H₂ and have significantly slower response times. However, in Pd/Ni alloy films (>8% Ni), H₂S has negligible effect [11].
2.4 Selective-permeable Layers

As discussed in the previous section, Pd and Pd/Ni based hydrogen sensors are affected by other gases. One of the ways to remedy this is to use selectively permeable layers to prevent other gas molecules from reaching the Pd or Pd alloy metal surface. Hydrogen, being the smallest molecule, diffuses through many materials. Commercially, Pd membranes, maintained at high temperatures, are used to separate or purify H₂ gas. This is possible due to the high diffusivity of H₂ through Pd (Figure 2.1). Ceramic membranes (Nanosil) [29], nanoporous carbon membranes (developed by Air Products & Chemicals Inc.) [30,31] and some fluorocarbon polymers also have good selectivity for H₂. There is a small body of literature on polymeric and porous membranes (ceramic) for separation of hydrogen from gas mixtures [32–35]. Hughes et al [34, 35] have demonstrated the effectiveness of silica membranes (sol-gel chemistry) in mitigating the effects of O₂, NO and H₂S. Various forms of SiO₂ have been known to have different permeabilities for different gases like O₂, He, Ar, H₂, etc. [36–38]. Among the gases H₂ and He have by far the highest diffusivities [39] (see appendix C). In fact, SiO₂ (amorphous) has been explored for barrier applications against O₂ and moisture in the food packaging and medical device industry [38,40,41]. The difference in gas diffusivities in SiO₂ could also be used to separate H₂ from gas mixtures for improving H₂ detection in gas mixtures.

SiO₂ (thermally grown, silica glass) has long been known to be permeable to H₂ [36,39, 42–44]. Unlike the membrane materials described earlier, SiO₂ is not a porous media (micrometer sized voids) and gas separation is achieved by taking advantage of differences in diffusivity of H₂ and other gases in SiO₂. There are numerous theories proposed to describe the structure of amorphous SiO₂; prominent among them are the continuous random network model (CRN), microcrystalline model and strained mixed cluster model (SMC) [1,45]. The CRN model, originally proposed by Zachariasan (1932) [46], assumes the oxide to be a random chain composed of tetraheadral units (SiO₄) sharing the corners with adjacent tetraheadrons. In this chain, the Si–O–Si bond angle is assumed to vary. In the microcrystalline model, originally proposed by Randall et al [47], the oxide is assumed to consist of microcrystalline grains (slightly larger than a unit cell) of different types of crystalline SiO₂, separated by interconnecting region. The SMC model is similar to the microcrystalline model and was originally proposed by Goodman (1985) [45]. According this model, the oxide consists of quasi-crystalline polymorphic clusters (∼3 nm in diameter), linked at the boundaries by strained interfaces. In most cases, the behavior of the oxide is readily described by a combination of these theories.
Diffusion of gas molecules in a non-porous media occurs by execution of size-dependent jumps within the media. These jumps are controlled by the activation energy needed to create transient gaps of appropriate size for the jump to occur. This activation energy is lower for smaller molecules, and, hence favors its diffusion. This selective process is called “energetic selectivity” [48]. In SiO$_2$, diffusion of H$_2$ is thought to occur through a series of jumps in the interstitial sites (locations within rings in amorphous SiO$_2$). This process is controlled by the activation energy for the jump. Gibson and Dong [49] suggest that voids of ~1 nm diameter are present in amorphous SiO$_2$. Voids of this size can be formed in absence of broken bonds, due to formation of rings of Si–O–Si chains [1]. These voids could assist in diffusion of gas molecules. Molecular dynamics simulation studies [50] of H$_2$ diffusion in various forms of SiO$_2$ indicate that this process also results in trapping of hydrogen molecules in certain sites (sinks) due to formation of metastable states with the Si and O atoms. This is consistent with the fact that SiO$_2$ absorbs H$_2$ and traps it in the bulk. Experimentally, diffusion of H$_2$ through quartz (crystalline SiO$_2$) has been demonstrated in a series of experiments conducted by Lee et al [42,43]. Their work indicates that the process is not purely diffusion controlled, but moderated by solubility of H$_2$ in quartz. Studies on MOSFETS (metal oxide field effect transistors) conducted by Mrstik et al [44] also indicate that H$_2$ diffuses rapidly through thermally grown oxides. Measured diffusivities of gas molecules thermally grown SiO$_2$ (amorphous) indicate that diffusivity of H$_2$ is orders of magnitude larger than that of other diatomic gases [39] (appendix C), and, hence can be used as a selective barrier layer to separate H$_2$ from other gas molecules of larger atomic (molecular) size.
References


Chapter 3

Sensor Design and Fabrication

Thin film sensors were fabricated using conventional CMOS (complementary metal oxide semiconductor) fabrication techniques. These sensors are based on the “robust hydrogen sensors” developed by Sandia National Labs [1, 2]. Palladium and palladium alloy thin film resistors (chemiresistors) were used to detect hydrogen over a wide range of concentrations. In this chapter, the process used to fabricate chemiresistors is described in detail. Unlike the work done at Sandia using evaporation techniques, magnetron sputtering was used for depositing the active metal (Pd and Pd/Ni alloy) in these sensors.

3.1 Design Considerations

The sensor design incorporated resistor elements that would facilitate understanding the sensor characteristics and mechanisms of Pd based thin film chemiresistors. The following important factors affecting the sensor performance were studied.

Geometry: Resistor structures with different perimeter to area ratio, edge to area ratio, active to non-active area and film thickness.

Alloy composition: Pd/Ni alloy films with different compositions.

Morphology: Films with different micro-structure deposited under different conditions.

Adsorption of hydrogen by Pd is a surface process, hence the effect of the surface area and perimeter of the resistor was studied by varying the resistor geometry. The sensor
test structure die incorporated resistor elements with different surface area, surface area to perimeter ratio and non-active surfaces. These test structures also included structures that would have approximately the same resistances for different film thickness. Figure 3.1 shows some of the sensor structures that were investigated. To facilitate the study of geometric effects on sensor response and reliability (redundant resistors), each die had 4 to 6 resistor elements that could be monitored simultaneously. The resistor elements were connected to contact pads arranged in a circular manner (see Figure 3.2). The contact pads were arranged in this manner to conform to the probe head in the electrical characterization system. The probe head consisted of contact pins arranged in a circular manner on a ceramic ring. This made it possible to measure all of the 6 resistor elements simultaneously and to keep the size of the sensor die relatively small, \( \sim 1 \text{ cm}^2 \). A more detailed description of the measurement system is given in Chapter 5. Nominally all the resistor elements were designed to have a resistance of 1000 to 2000 \( \Omega \) (for a metal film 1000 \( \AA \) thick). Detailed images of the die with dimensions are listed in Appendix B.

### 3.2 Chemiresistor Fabrication

The sensors were fabricated on 3 inch, p-silicon (boron doped) wafers (\(<100>\)). A barrier layer of LPCVD silicon nitride (500 \( \AA \)) was deposited on the wafer to prevent trapping of \( \text{H}_2 \) by the silicon substrate. It should be noted that LPCVD silicon nitride has substantial amounts of hydrogen in the film but this does not seem to affect the sensor operation. The complete process flow is described pictorially in Figure 3.3. Before proceeding with the fabrication steps, the wafers were cleaned in acetone, IPA (Iso-Propyl Alcohol) followed by a rinse in DI (De-Ionized) water. The wafers were first dipped in acetone and agitated in an ultrasonic bath for about 2 minutes to remove organic impurities. This process was then repeated with IPA solution to remove traces of acetone. The wafers were subsequently rinsed in DI water and blow-dried in compressed nitrogen. Finally, the wafers were baked on a hot plate at 115\(^{\circ}\)C for about 5 minutes to get rid of moisture from the surface.

#### 3.2.1 Lithography and Lift-off Process

The cleaned and dried wafers were patterned using standard photo-lithography techniques. HMDS (Hexamethyldisilazane), an adhesion promoter, was spun on the wafer to improve the adhesion of photoresist on to the nitride coated wafer. Shipley 1813 was the photoresist of choice for patterning the hydrogen sensors. The photoresist was spin coated onto the
Figure 3.1: Geometry of some of the chemiresistor structures in the sensor die.

Figure 3.2: Image of one of the sensor die.
wafer with a spinner operating at 4000 rpm (for 40 s). The resist was then baked at 115°C for 15 seconds to eliminate excess solvent (soft bake). The wafer was subsequently soaked in chlorobenzene for 20 minutes and blow-dried using compressed nitrogen. This soak reduces the dissolution rate of the photoresist in the layers exposed to chlorobenzene – an essential factor for achieving the “overhang” (see Figure 3.4) in features for the “lift-off” process [3,4]. Formation of overhang is important for creating discontinuities in the films deposited on photoresist. The recommended soak time is 5 to 15 minutes, however longer soak time would increase the thickness of the overhang. Subsequently, UV exposure times had to be increased to compensate for the loss of sensitivity of photoresist soaked in chlorobenzene. The wafer was subsequently patterned using mask 1 (contact pads) or mask 2 (resistor lines). Karl Suss MA6 contact aligner was used to pattern the photoresist (365 nm UV) (Figure 3.5). A 10 second exposure at 12 mW/cm² with vacuum contact was found to be optimal for good pattern transfer. Exposure times ranging from 7 to 12 seconds did not produce any noticeable difference in pattern transfer. The exposed wafer was developed in dilute MF-312 solution (1:1 MF-312 and DI water). The development times varied from ~2
Figure 3.4: SEM image of the overhang after chlorobenzene soak.

to ~5 minutes. The development process was terminated by visually observing the pattern. It should be noted that this process was not reproducible since the development time varied from ~2 to 5 minutes. The wafer was not hard baked as this process resulted in distortion of the pattern. The same lithography steps were employed for transferring the pattern from

Figure 3.5: Schematic of the process flow for “lift-off” process.

mask 2 (contact pads) and mask 1 (resistor lines).
3.2.2 Metallization

A combination of evaporation and sputtering was used to deposit the metal films. The metal films were patterned by the “lift-off” process. This method was chosen because there is no known method to pattern Pd metal thin films by selective dry etching. Aluminum was used for contact pads and Pd/Pd-Ni alloys were used for resistor lines. Sputtering was used to deposit Pd and Pd/Ni alloys. An adhesion layer of chromium (Cr), ∼200 Å was used to improve adhesion of Al and Pd on the nitride surface. This is necessary because unlike Cr, Pd does not form a stable nitride and, hence, does not adhere well to Si₃N₄ [5]. Cr was deposited by e-gun evaporation and the Al contact pads was deposited by evaporation using a thermal source.

Contact-pad Metallization

An evaporation system from Kurt J. Lesker with both thermal and e-gun source was used for evaporating Cr (adhesion layer for contact pads and resistor lines) and Al (contact pads). The system was pumped to a base pressure of ∼5×10⁻⁶ torr by a cryo pump. The pressure during the evaporation process was ∼10⁻⁵ torr. The deposition rate and film thickness were monitored by a crystal thickness monitor. Pellets of 99.95% metal pellets (Al and Cr) were used as the metal source. For contact pad deposition, a 200 Å thick film of Cr was deposited, followed by a 1500 to 2000 Å thick Al film. Both films were deposited without breaking vacuum. Subsequently, the wafer was patterned using mask1 (resistor lines). A 200 Å thick Cr film was deposited on the patterned wafer. The wafer was then cleaved into ∼1 inch square pieces (4 dies) for Pd or Pd-Ni alloy film deposition.

Palladium and Palladium-Nickel Alloy Deposition

Palladium thin films were deposited in a cylindrical vacuum chamber 25 cm in diameter and 20 cm in height with a balanced magnetron sputter gun 2 inch in diameter. The target material used is a 2 inch diameter and 1/8 inch thick palladium metal (99.5%). This source could deposit a uniform film over an area of ∼1 inch diameter, hence the wafer had to be cleaved into ∼1 inch square pieces. The target to substrate distance was maintained at 100 mm. The Pd target was oriented at ∼45° off the normal to the substrate (see Figure 3.6). The chamber was pumped to a base pressure of ∼5×10⁻⁷ torr by a cryo pump (CTI 8 cryo pump). Argon gas was fed into the system through a mass flow controller. The pressure was set by fixing the flow rate and manually controlling the valve used to isolate.
the cryo pump from the chamber. An Advanced Energy MDX-1K DC power source and an ENI RPG-50 pulsed DC source were used for thin film deposition. The source and the substrate were monitored with an oscilloscope (HP 54603B).

**Plasma Characterization Set-up**

The sputter discharge was studied by an EQP (energy and quadrupole) mass spectrometer from Hiden Analytical [6]. In this mode the magnetron source was relocated to a different port in the chamber as seen in Figure 3.7. In this new arrangement it was ensured that the EQP probe tip was located at a distance of 100 mm from the magnetron source, an identical orientation as the thin film deposition arrangement. A 100 µm orifice was used by the probe to sample the ions and neutrals from the plasma. The probe tip was electrically floating in this configuration. A detailed analysis of the energy distribution of the incident ions that comprise the deposited metal film is presented in chapter 4.

### 3.2.3 Semi-permeable Coating – Silicon dioxide

SiO$_2$ was deposited by reactive pulsed DC sputtering from an electrically conducting SiC target doped with graphite$^1$ [7]. The sputter system was the same as used for Pd deposition. Here, the SiC target was located normal to the substrate (see Figure 3.6). A 15% oxygen and argon gas mixture at 10 mtorr total pressure was used for deposition. The pulsed DC source was operated at 100 W, 680 nm pulse width and 160 kHz frequency. Under these conditions, the carbon from the target is burned by the oxygen ambient resulting in near stotiometically pure SiO$_2$. The quality of the oxide was verified by FTIR and optical spectrometry.

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$^1$HexoloySG from Carborundum(Saint-Gobain)
Figure 3.6: Schematic of the deposition chamber showing the relative positions of the source and substrate.

Figure 3.7: Schematic of the chamber for the IEDF measurements using mass spectrometer.
References


Chapter 4

Thin Film Morphology and Plasma Characterization

Physical vapor deposition (PVD) techniques such as sputtering offer a convenient way to deposit thin films with varied morphology. In this thesis, gas pressure, ion bombardment and alloying have been used to control the morphology of Pd and Pd/Ni thin films. The sputter discharge has been characterized so as to relate the ion energy directly to ion bombardment and indirectly to the resulting thin film morphology.

4.1 Introduction

Sputtering refers to the process of removing material by collision between a projectile and a target. The energetic projectile dislodges atoms from the target as a result of collisions. This process is discussed briefly in following paragraphs. An extensive discussion of the process and current trends is available in several review articles [1–4].

In the physical sputtering process energetic particles (usually ions), generated by a plasma, strike a target, thereby ejecting atoms from the surface. The process is governed by the energy of the projectile and mass ratios of the incident ion and the target atom. Collisions due to low energy ions (< 10 eV) result in little or no ejection of target atoms due to insufficient energy to break near surface (≤ 3 nm) bonds. Ions with much higher energy (in excess of few keV) penetrate beyond the target surface causing considerable damage to the target but results in ejection of very few target atoms. However, ions of moderate energy
(hundreds to few thousand eV) can create a substantial number of broken bonds close to
to the surface and, hence, ejection of a large number of target atoms.

Sputtering yield (number of target atoms emitted per incident ion) is commonly used to
characterize sputtering and is directly related to the deposition rate of the target material at
the substrate. It is between 0.5 and 2 for most materials sputtered by argon ions (Ar \(^+\)). It
increases steadily for ion energies in excess of few eV and saturates at few hundred eV [2,5].
Since the ion energy is proportional to the voltage applied to the target (cathode) and the
bombarding flux (current) scales directly with sputter rate, the deposition rate scales with
the input power. This makes it possible to deposit films of any stoichiometry using multiple
targets simultaneously. The emission profiles of sputtered atoms typically follow a cosine
law distribution, implying that the emission rate at some angle off from the normal to the
target is equal to the cosine of the emission angle times the emission rate normal to the
target. Thus the uniformity of the film deposited is dependent on the orientation of the
target and the substrate and the relative areas of the target and substrate. Typically, the
target should be double the size of the substrate (stationary) to obtain a uniform film.

Thin films (coatings ≤ few µm thick) deposited by sputtering can have a broad range of
microstructures (sometimes referred to as morphologies). The microstructure depends on
the way the target atoms condense on the substrate and often upon their surface diffusion.
Neutral/ion bombardment and substrate temperature affect the surface diffusion process in
PVD process and, hence, the microstructure. The Structure Zone Model (SZM) relates the
microstructure of PVD thin films to deposition conditions like pressure, ion bombardment
and temperature. The model, originally formulated by Movochan-Demchishin [6] for evap-
oration process without bombardment effects, described 3 types of microstructure: zone 1
(low or negligible surface diffusion – cauliflower-like), zone 2 (significant surface diffusion
– faceted top surface) and zone 3 (bulk diffusion – eqi-axed grains) corresponding to in-
creasing substrate temperature. Subsequently, Thornton [7] modified the model to include
the effect of ion/neutral bombardment (proportional to gas pressure) on the microstructure
and added a transition zone, zone T between zone 1 and zone 2. Zone T morphology has a
relatively featureless, smooth top surface, occurs at the low surface diffusion condition and
completely replaces the zone 1 morphology at higher ion bombardment (lower gas pressure)
conditions. Messier et al [8] further refined the SZM to describe the evolution of the film
morphology as the film is grown. This model explains the growth evolution of void-column
morphologies from the nm to µm scales for films of thickness of the on the order of a
micrometer. Palladium thin films studied here, conform to these models.

EQP (energy and quadrupole) mass spectrometer is a simple tool for measuring the energy
distribution of ions and performing mass analysis of the constituents (ions and neutrals) of the plasmas. This tool samples the plasma through small orifice (100 to 150 μm) and determines the energy distribution of ions of a specified mass. Hence, this tool is useful in providing information about the composition of the plasma and the ion bombardment at the substrate. By sampling the plasma at the substrate (using EQP) for magnetron sputter discharge, this tool can provide information about ion bombardment at the substrate. SEM (scanning electron microscopy) imaging (surface and cross section) of deposited thin films, provides a simple way to characterize their morphology for thickness in excess of 2000 Å. Here, IEDF (ion energy distribution function) data in conjunction with SEM micrographs of thin films have been used to understand the effect of ion bombardment on the morphology. Like process pressure, use of bipolar asymmetric pulsed DC source alters the IEDF which in turn effects the film morphology.

4.2 Experimental Details

Palladium thin films were deposited in the sputter system described in the previous chapter. The target material used was 2 inch diameter and 1/8 inch thick palladium metal (99.95%, from Refining Systems Inc, Las Vegas, Nevada, USA). The target to substrate distance was maintained at 100 mm. The Pd target was oriented at ∼45° off the normal to the substrate (see Figure 3.6). The chamber was evacuated (high 10⁻⁷ torr) and back filled with argon gas, introduced into the system through a mass flow controller. The pressure was set by fixing the flow rate and manually controlling the valve used to isolate the cryo pump (CTI 8 cryo pump) from the chamber. An Advanced Energy MDX-1K DC power source and an ENI RPG 50 pulsed DC power source were used for thin film deposition. The source and the substrate voltages were monitored by an oscilloscope (HP 54603B).

The films were deposited on silicon nitride film (LPCVD, ∼500Å) deposited on a boron doped (p-type) <111> silicon substrate at pressures of 5, 10 and 25 mtorr. The Pd target was supplied with a constant input power of 20 W. The typical currents and voltages under these conditions are shown in table 4.1. It should be noted that the power values indicated here are those set on the power source and not measured at the target. There is a discrepancy in the set power (20 W) for DC source and the calculated power (∼30 W) from the voltage and current values displayed by the power supply. This is attibuted to minor calibration issues with the power supply. For sake of consistenc, the set power values (indicated by the display on the power source) have been used in all the experiments and discussions. For morphological studies, ∼1000 Å and ∼3000 Å thick Pd films were deposited. The film
Table 4.1: Parameters of the input power source for Pd deposition.

<table>
<thead>
<tr>
<th>Source</th>
<th>Pressure (mtrr)</th>
<th>Power (W)</th>
<th>Voltage (V)</th>
<th>Current (mA)</th>
<th>Frequency (kHz)</th>
<th>Pul. width (µm)</th>
<th>Duty cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>5</td>
<td>20</td>
<td>328</td>
<td>86</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>10</td>
<td>20</td>
<td>320</td>
<td>97</td>
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<td>25</td>
<td>20</td>
<td>310</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>pul. DC</td>
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<td>20</td>
<td>171</td>
<td>110</td>
<td>145</td>
<td>440</td>
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<td></td>
<td>25</td>
<td>20</td>
<td>150</td>
<td>130</td>
<td>145</td>
<td>440</td>
<td>48</td>
</tr>
</tbody>
</table>

In magnetron sputtering – DC Source

In sputtering with a DC power source, the target is maintained at a constant potential. The ions from the plasma traverse the plasma sheath, gain energy and sputter the target atoms. This process can be enhanced by confining the plasma to regions close to the target thereby producing higher ion flux at the target. The confinement is achieved by using a toroidal magnetic field looping around the target (field lines originating and ending at the target surface). This method is referred to as magnetron sputtering. The localized bombardment of the target in magnetron sputter source enables enhanced deposition rates at cathode voltages of a few hundred of volts. Broadly, magnetron sputtering is classified as balanced and unbalanced. Balanced magnetron sputtering refers to confinement of the magnetic field

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1 www.leo-em.co.uk
2 www.hiden.co.uk
lines to the target in a closed loop. In unbalanced magnetron sputtering, the magnetic field spreads out from the target toward the substrate. In this work a balanced magnetron sputter source has been employed. Use of DC power source limits this process to electrically conducting targets.

4.3.1 Palladium Thin Film Morphology

The SEM images of films deposited at 5 mtorr and 20 W power, (Figures 4.1 and 4.2) indicates a densely packed columnar structure. The top surface of these films appear to be smooth (±2 nm) as indicated by the AFM images (Figures 4.3 and 4.4) and the columns are of uniform diameter (10 to 20 nm). The substrate temperature during the deposition process was ~310 K. Hence, the structure of the film is well within zone 1/zone T (melting point of Pd ~ 1800°C, T/T_m ≈ 0.17) of SZM. At 5 mtorr gas pressure, the film’s structure falls into zone T (smooth top surface, dense columnar structure) as predicted by SZM. For the same input power, but a higher gas pressure of 25 mtorr, the films exhibit less dense columnar structure with well defined boundaries (see Figures 4.5 and 4.6). The columns are larger and faceted. These films have substantially rougher surface (±7 nm) when compared to the 5 mtorr films as indicated by the AFM images (see Figures 4.7 and 4.8). This film morphology corresponds to zone 1 in SZM. The substrate temperature during deposition of these films was measured to be ~310 K. Hence at 25 mtorr, the films indeed fall into zone 1. The transition of film morphology from zone T to zone 1, as the deposition pressure increases from 5 mtorr to 25 mtorr, is clearly seen in Pd films deposited at 10 mtorr (Figures 4.9 and 4.10). These films show features seen in both 5 mtorr and 25 mtorr films, namely, smooth densely packed columns and large faceted columns with rough surface, in localized areas. A closer examination of the structure of the films deposited at pressures of 5 mtorr and 25 mtorr indicates that the large faceted columns appear to have a layered finer structure (stack of planes).

X-ray diffraction data (see Figure 4.11) for these films indicate no preferred orientation (the ratios of the intensities of the different peaks match those available in the database\(^3\) for randomly oriented powder standards). The spectra shows hardly any variation in the FWHM (full width half maximum) of the \(<111>\) peak for films deposited at pressures of 5, 10 and 25 mtorr. Using Scherrer equation [9] the crystallite diameter was computed to be approximately 135 to 150 Å for all the films. This indicates that the change in pressure results in a change in the column size but not the crystallite size. This indicates that the columns are not monolithic, but are composed of finer structures. It should be noted that

\(^3\)JCPDS-International Center for Diffraction Data
Figure 4.1: SEM micrograph of Pd film ~3400Å thick, deposited at 20 W DC power, 5 mtorr Ar gas pressure.

Figure 4.2: SEM micrograph of the same film with 45° tilt (20 W DC power, 5 mtorr pressure).
Figure 4.3: AFM surface scan (3D) of Pd film ~625Å thick (20 W, 5 mtorr Ar gas pressure).

Figure 4.4: AFM image with surface roughness of Pd film ~625Å thick (20 W, 5 mtorr Ar gas pressure).
Figure 4.5: SEM micrograph of Pd film \(\sim 2700\text{Å}\) thick, deposited at 20 W DC power, 25 mtorr Ar gas pressure.

Figure 4.6: SEM micrograph of the same film with 45° tilt (20 W DC power, 25 mtorr pressure).
Figure 4.7: AFM surface scan (3D) of Pd film ~1030Å thick (20 W DC, 25 mtorr).

Figure 4.8: AFM image with surface roughness of Pd film ~1030Å thick (20 W, 25 mtorr).
Figure 4.9: SEM micrograph of Pd film ∼3500Å thick, deposited at 20 W DC power, 10 mtorr Ar gas pressure.

Figure 4.10: SEM micrograph of the same film with 45° tilt (20 W DC power, 10 mtorr pressure).
the measured stresses of the films were in the MPa range which produce minimal effect on the XRD (x-ray diffraction) spectra. Hence stress effects were not accounted for in the calculation of crystallite size.

Figure 4.11: X-ray diffraction spectra of Pd thin films deposited at 5, 10 and 25 mtorr and 20 W DC power.

4.3.2 Ion Energy Distribution Function of Ar$^+$ and Pd$^+$

IEDFs of Ar$^+$ and Pd$^+$ for DC magnetron sputtering were measured in the range of -10 to 90 V and at pressures of 5 and 10 mtorr (Figure 4.12). These measurements indicate narrow peaks (FWHM of around 10 V) centered around 0 V. The peak signal intensity for Pd$^+$ was about an order of magnitude below that of Ar$^+$. Also, the shape of the peak did not alter with changes in sputtering gas pressure, indicating that the sheath at the substrate did not undergo any significant change as the process pressure increased from 5 to 10 mtorr. Since the substrate (anode) is floating, it would be at a slightly negative potential [10]. Since the plasma potential of the discharge is only a few volts, the ions drifting toward the substrate would see very small potential drop across the sheath at the substrate. Also, the ions emitted from the cathode would be thermalized (mean free path at pressures of few mtorr is less than 5 cm, assuming the collision cross section to be in $10^{-15}$ - $10^{-16}$ cm$^2$ range) in the plasma before reaching the substrate ($\sim$100 mm from the cathode). Thus, ion bombardment effects would be minimal at the substrate and should have negligible effect on the morphology of the thin films. This is seen in the IEDF data (Figure 4.12) that indicates that most of the ions reaching the substrate have energies close to 0 eV at both 5 and 10 mtorr pressures. The variation in the morphology for the films deposited at 5 and
10 mtorr is thought to be due to bombardment of the substrate by energetic neutral atoms (Pd and Ar). It should also be noted that at these low pressures (5 to 20 mtorr) the sheath may not be completely formed and hence the ions reaching the substrate does not see the complete potential drop across the sheath.

![Figure 4.12: IEDF of Ar\(^+\) and Pd\(^+\) ions at 5 mtorr and 10 mtorr DC magnetron sputtering discharges.](image)

Energetic neutrals have long been known to play an important role in the morphology of sputter deposited thin films [11–14]. The energy transferred to the target atom is dependent on the ratio of the mass of the impinging atom (Ar) to the target atom (Pd), with the maximum energy transfer occurring when the masses of the impinging and the target atoms are the same. For lighter impinging atoms, energy transfer is reduced and the number and energy of reflected neutrals increases. Here, the Ar atom (40 amu) is light when compared to the Pd atom (106 amu), hence collisions between Ar and Pd atoms would result in energetic reflected neutral atoms. A change in pressure from 5 to 25 mtorr results in a decrease of the mean free path of neutral atoms by a factor of \( \sim 2.2 \). In other words the atoms will suffer five fold increase in number of collisions traversing the distance between the target and substrate. Hence the energy of the neutral atoms bombarding the substrate would be substantially larger at 5 mtorr than at 25 mtorr. This could possibly account for the difference in the morphology of Pd thin films deposited under these conditions.
4.4 Magnetron Sputtering – Pulsed DC Source

In the last decade, a great deal of attention has been given to pulsed DC magnetron sputtering [15–17]. This technique enables high rates of reactive gas sputtering of insulating materials when compared to an rf power source. Generally, pulsed DC sources are classified as unipolar (cycling between 0 and a negative voltage, at 10 to 300 kHz range) or bipolar (cycling between positive and negative potential, at 10 to 300 kHz range). In deposition of insulating thin film by reactive sputtering using pulsed DC source, during the negative pulse (deposition cycle), parts of the target gets covered by insulating film (target poisoning) leading to a build-up of positive charge, which could result in arcing. The positive pulse cycle eliminates the built-up positive charge and cleans the target. The higher mobility of electrons ensures that the positive cycle be around 10 to 20% of the total duration of the pulse cycle [15]. Thus higher deposition rate (compared to rf source) is achieved without arcing.

In this work, an asymmetric bipolar pulsed DC source from ENI (20 W, 145 kHz, 440 ns) was used to deposit Pd films on a floating (electrically) silicon/silicon nitride substrate. Under these conditions the duty cycle was around 50%. The input signal at the source and at the substrate were measured by an oscilloscope (Figure 4.13). This source does not supply uniform negative potential to the target (cathode), but a time varying voltage reaching a maximum of about -400 V at 20 W power. In the positive cycle of the pulse, the voltage oscillates before attaining a steady state at around 85 V. The oscillations at the source varied from about 300 V to about -100 V and lasted for about 50% of the time period of the positive cycle. During this part of the cycle the plasma potential would increase to just over 85 V. Since the substrate is electrically floating, it follows the plasma potential. The potential of the floating substrate was measured to be around 60 V with respect to the ground potential. In the negative part of the pulse, the anode potential was measured to be slightly negative, as is the case for floating-wall potential of a glow discharge [10]. This behavior is independent of the target material and has been observed when other target materials like Zn, Ni, SiC, etc have been used. The input pulse shape seems to be solely dependent on the power source and pulse shape [18]. The pulse shape was found to be independent of the pressure, frequency and pulse width.
Figure 4.13: Schematic of the measured input signal at source and the output signal at the floating substrate for a pulsed DC power source running at 20 W, 145 kHz frequency and 440 ns pulse width.

4.4.1 Palladium Thin Film Morphology

SEM images (Figure 4.14 - 4.17) of films deposited using a pulsed DC source indicates a denser and more facetted morphology when compared to DC sputter deposited films under the same pressure and power. The films deposited at 5 mtorr clearly show facetted columns. A closer examination of the facetted columns indicates that the facets are composed of a stack of planes. X-ray diffraction data (see Figure 4.18) indicates that these films are polycrystalline and do not have any preferred crystallographic orientation. A lower magnification image (Figure 4.19) of film deposited using a pulsed DC source shows a large number of facetted columns oriented at \( \sim 45^\circ \) off the normal to the surface. It should be noted that the sputter target is \( 45^\circ \) off the normal to the substrate as described in the experimental setup (see Figure 3.6). The off normal (to the substrate) location of the target during sputtering ensures that the flux of ions bombarding the substrate would predominantly be \( 45^\circ \) off the normal to the substrate. This oblique incidence of the ions would cause the columns in the film to grow at an angle, towards the direction of the ion bombardment (tilt effect).

4.4.2 Ion Energy Distribution Function of \( \text{Ar}^+ \) and \( \text{Pd}^+ \)

IEDF measurements of the pulsed DC discharge indicates two narrow peaks (FWHM of about 5 V), one at around 5 V and another peak at around 65 V with ions distributed at intermediate energies (Figure 4.20). This distribution can be attributed to the asymmetric
Figure 4.14: SEM micrograph of Pd film \(\sim2700\text{Å}\) thick, deposited at 20 W pulsed DC power, 5 mtorr Ar gas pressure.

Figure 4.15: SEM micrograph of the same film with 45° tilt (20 W pulsed DC power, 5 mtorr Ar gas pressure).
Figure 4.16: SEM micrograph of Pd film ∼1650Å thick, deposited at 20 W pulsed DC power, 25 mtorr Ar gas pressure.

Figure 4.17: SEM micrograph of Pd film (∼2950Å) film with 45° tilt (20 W pulsed DC power, 25 mtorr Ar gas pressure).
Figure 4.18: X-ray diffraction spectra of Pd thin films deposited at 5 mtorr pressure, 20 W DC and pulsed DC power.

Figure 4.19: SEM micrograph of the same film with 45° tilt (20 W pulsed DC power, 5 mtorr Ar gas pressure).
pulsing of the input power. When the cathode reverses its polarity from around -400 V to positive voltage (oscillations followed by a steady voltage of $\sim 85$ V), the plasma potential changes rapidly due to a sudden change in the boundary conditions of the discharge. This increase in plasma potential results in an increase in the substrate potential, as seen in Figure 4.4.2. Measurements and simulations made by Budtz-Jørgenson et al [19] on temporal evolution of unipolar pulsed DC plasmas, indicate that the plasma potential increases by as much as the cathode voltage ($\sim 200$ V for a cathode voltage of -400 V) when the cathode is grounded (0 V, unipolar pulsed DC source). This large increase in plasma potential was mirrored by the rapid rise in flux of energetic positive ions. The plasma potential and the ion flux gradually decays, in the case of a grounded substrate (anode). However, in the case of a floating anode, the anode potential follows the plasma potential. For a collisionless sheath at a floating anode, the voltage drop across the sheath ($\Delta V$) is given by [10]

$$\Delta V = T_e \ln \left( \frac{m_{Ar}}{2\pi m_e} \right)^{1/2}$$

where $T_e$ is electron temperature, $m_{Ar}$ is the mass of argon atom and $m_e$ is the electron mass. Assuming that the electron temperature of the plasma is around 3 eV, the potential drop across the sheath would be around 12 V. Hence, in the negative part of the pulse, the anode potential would have a small negative value (Figure 4.4.2). As the substrate (anode) is 100 mm from the target, the assumption of a collisionless sheath may not be valid, hence the ions traversing the sheath lose energy in collisions before reaching the substrate. Langmuir probe measurements made by Bradley et al [18] on asymmetric pulsed
DC magnetron (unbalanced), close to the anode, indicate that the floating potential indeed follows the plasma potential rises to a positive value when the cathode is in the positive part of the pulse and drops to a slight negative value in the negative part of the pulse.

Figure 4.21: Schematic of the measured input signal at source and the output signal at the floating substrate for a pulsed DC power source.

Figure 4.22: Schematic of the variations in the plasma potential in balanced magnetron sputter discharge using pulsed DC source [19].

The change in the cathode voltage from $\sim 400$ V to $\sim 300$ V and the subsequent jitter in the voltage (lasting for $\sim 1000$ ns, a characteristic of the pulsed power source) results in a sudden rise in the plasma potential that is not uniform across the plasma (from cathode to anode). This increase in the plasma potential also raises the substrate potential (Figure 4.4.2). The increase in the plasma potential and the floating potential results in bombardment of the substrate (anode) by energetic positive ions, as seen by the peak centered at $\sim 65$ eV in the time averaged IEDF of the sputter discharge at 5 mtorr (Figure 4.20). The positive pulse applied to the cathode stabilizes at $\sim 85$ V and remains at that voltage for around 550 ns. The floating substrate potential follows the cathode potential and attains a constant potential of $\sim 60$ V corresponding to the constant $\sim 85$ V at cathode. Subsequently, the cathode voltage drops to 0 V and then to $\sim 400$ V. The floating substrate potential also drops from $\sim 60$ V to 0 and then $\sim 1$ V during the same period. This change, constant potential to a negative potential at the floating substrate, results in bombardment of the substrate by ions with a wide distribution of energies ($\sim 10$ eV to $\sim 60$ eV), as seen in the time averaged IEDF of the sputter discharge at 5 mtorr (Figure 4.20). When the cathode is at negative potential (reaching a maximum of $\sim 400$ V), the floating substrate is at a constant negative potential of $\sim 1$ V and the plasma potential remains constant at a few volts. The low energy peak centered at $\sim 5$ eV in the time averaged IEDF for positive ions is associated with the potential drop across the sheath in this phase (Figure 4.20).
Variations of pulse frequency and pulse width\(^4\) of the pulsed DC source has a small effect on the location of the peaks in IEDFs (Figures 4.23 and 4.24). The energies associated with the peaks in the IEDF are only dependent on the voltages associated with the input pulse at cathode, while the width of the peaks in the IEDF are dependent on the duration of the different phases on the pulse cycle. The voltages associated with the various phases of the pulsed DC voltage did not change significantly as a function of pulse frequency and pulse width, hence it did not alter IEDF of the positive ions bombarding the substrate. As indicated earlier, at these low pressures (5 to 25 mtorr) the plasma sheath may not be well defined. This is supported by the fact that the films have facets indicating that the substrate experiences oblique bombardment of ions as opposed to normal incidence in case of well formed sheath (the sheath should take the substrate surface profile for features larger than the Debye length).

4.5 Palladium Thin Film Morphology – Effect of Alloying Nickel

The alloy films were deposited by co-sputtering Pd (DC source) and Ni (pulsed DC source). The alloy composition was determined by the sputter rates of Pd and Ni. The sputter rate is dependent on the input power, among other deposition conditions (pressure, etc.). As discussed earlier, the sputter rate is directly related to the input power: hence, by altering the power ratio (input power to Pd/ input power to Ni), it is possible to change the amount of Ni in the film. This is verified by x-ray diffraction data. Figure 4.25 shows the shifting of the peak corresponding to \(<111>\) planes with increasing amounts of Ni. For pure Pd films the \(<111>\) peak occurs at a \(2\theta\) value of 40.1\(^\circ\). This is in agreement with the spectra for Pd standard (40.113\(^\circ\)\(^5\). As the Ni content of the film increases, the peak shifts towards \(2\theta\) value of 44.5\(^\circ\), the location of \(<111>\) peak for Ni. This indicates that the co-sputtered films are indeed alloys as the spectra is derived from a large area (spot size of the X-ray beam) and, hence, corresponds to the average composition of the whole area and not localized areas. The position of the peak (\(2\theta\) for \(<111>\)) is proportional to the percentage of Ni in the thin film (Figure 4.26), as predicted by Vegard’s law \([9]\). The composition of Pd/Ni alloy (10% Ni) films was also verified by electron microprobe technique.

Like Pd, nickel (Ni) is a group VIII transition metal and has a fcc lattice structure. It is completely miscible in Pd and forms a binary solid solution, implying that the alloy has

\(^4\)pulse width refers to the time period of the constant voltage during the positive part of the pulse cycle

\(^5\)JCPDS-International Center for Diffraction Data
Figure 4.23: IEDF of Ar\(^+\) and Pd\(^+\), deposited at 20 W pulsed DC power and 10 mtorr Ar gas pressure as a function of pulse frequency at 440 ns pulse width.

Figure 4.24: IEDF of Ar\(^+\) and Pd\(^+\), deposited at 20 W pulsed DC power and 10 mtorr Ar gas pressure as a function of pulse width at 145 kHz pulse frequency.
Figure 4.25: X-ray diffraction spectra of Pd/Ni alloy thin films with different Ni content deposited at 5 mtorr Ar gas pressure.

Figure 4.26: Shift in \(<111>\) peak as a function of Nickel concentration in thin films (Vegard’s law).

A single phase for all concentrations of Ni. Pd-Ni alloys are substitutional solid solutions. Being a smaller atom (Ni atomic radius - 1.53Å) when compared to Pd (atomic radius - 1.79Å), alloying Pd with Ni causes the lattice to contract [20]. This contraction of the lattice leads to a more compact microstructure, clearly seen in SEM micrographs of Pd/Ni alloy thin film (Figures 4.28 and 4.30). The micrographs indicates that the microstructure of Pd-Ni (10%) alloy at both 5 mtorr and 25 mtorr deposition pressures are denser than Pd thin films (Figures 4.2 and 4.6) deposited under same conditions. Also, the alloy films appear to be smoother than Pd films deposited under same power and pressure. However,
it should be noted that the Ni target was sputtered using a pulsed DC source. As discussed in the earlier sections, pulsing results in bombardment of the substrate by energetic ions which contributes to denser structure of the thin film.

IEDF measurements made on Ni target with a pulsed DC source yielded results similar those from Pd target. This suggests that the IEDF for positive ions is primarily a function of input power source conditions. It should be noted that IEDF measurements were not made in the co-sputtering mode (simultaneous operation of Pd and Ni targets) as the set-up for IEDF measurements allowed operation of one target at a time.

4.6 Summary

The morphology of Pd and Pd/Ni alloy thin films were found to be primarily dependent on the deposition pressure, energy of the ions bombarding the substrate and the alloying element. In DC magnetron sputter discharge, the morphology of the films were primarily governed by the deposition pressure, consistent with SZM. In the films studied here, increase in deposition pressure resulted in changes in the thin film morphology from smooth and dense columnar films (zone T) deposited at 5 mtorr to rough and large columnar films (prominent grain boundaries, zone 1) deposited at 25 mtorr. The target to substrate distance, being 10 cm, results in only low energy ions bombarding the substrate as indicated by measured IEDF of Pd$^+$ and Ar$^+$. The measured IEDF at 5 mtorr and 10 mtorr deposition pressure indicate peaks for Ar$^+$ and Pd$^+$ centered at $\sim$0 V. Changes in pressure cause no change in the location of the peaks or the width of the peaks in the IEDF of Ar$^+$ and Pd$^+$, indicating little change in the energy of the positive ions bombarding the substrate during film growth. Hence the changes in the morphology of Pd thin films grown at 5 mtorr, 10 mtorr and 25 mtorr are largely due to change in the energetic neutral bombardment of the substrate. This is consistent with the large body of literature that discusses the importance of neutral bombardment on thin film morphology in sputter discharge [11–14].

In magnetron sputtering with a pulsed DC source, the deposited Pd films were found to be smoother and denser than the films deposited by DC sputtering under same pressure and power conditions. This is attributed to overall increase in the ion energy of Ar$^+$ and Pd$^+$ bombarding the substrate, as indicated by the measured IEDF. The higher ion energy is due to the pulsing of the cathode to a positive potential, resulting in a dramatic increase in the plasma potential and hence, the floating potential. This increase in the plasma potential and the floating potential results in energetic ion bombardment of the substrate
Figure 4.27: SEM micrograph of Pd/Ni alloy film ~3800Å thick, deposited at 20 W DC power (Pd), 20 W pulsed DC (Ni), 5 mtorr Ar gas pressure.

Figure 4.28: SEM micrograph of the same film with 45° tilt (20 W DC power (Pd), 20 W pulsed DC (Ni), 5 mtorr Ar gas pressure).
Figure 4.29: SEM micrograph of Pd/Ni alloy film ~3400Å thick, deposited at 20 W DC power (Pd), 20 W pulsed DC (Ni), 25 mtorr Ar gas pressure.

Figure 4.30: SEM micrograph of the same film with 45° tilt (20 W DC power (Pd), 20 W pulsed DC (Ni), 25 mtorr pressure).
which results in denser films. The off axis location of the target (∼45° off the normal to the substrate) results in formation of faceted structures on the thin film. This also suggests that the sheath is not well formed as the ion bombardment is not normal to the substrate as is the case with well formed sheath.

Finally, alloying Pd with Ni, results in smoother and denser thin films. This is primarily attributed to the shrinkage of the Pd lattice, when Ni is alloyed with Pd (substitutional alloy).
References


Chapter 5

Sensor Characterization

Hydrogen sensors consisting of Pd and Pd/Ni alloy resistive elements (chemiresistor) were tested for their responses to hydrogen both in Ar and other gas mixtures (CO, SO$_2$). The chemiresistors were characterized as a function of resistor geometry, substrate temperature, total pressure, gas composition (H$_2$, CO), alloy composition and morphology. The effectiveness of protective coatings in counteracting the effect of competing gases was also evaluated.

5.1 Measurement Set-up and Procedure

A sensor characterizaton platform built at Sandia National Labs in Livermore, Ca specifically for this work was used to test chemiresistor. The test assembly consisted of a small chamber and a mounting for the sensor test head. The chamber was connected to a mechanical pump that could pump the chamber to the low torr pressure range. Gas mixtures were fed to the chamber through mass flow controllers. A RGA (residual gas analizer) was used to monitor the gas composition in the chamber. The volume of the chamber being small, ensured that changes in gas composition would stabilize in a short time period. The chamber pressure was controlled by a pneumatic butterfly valve connecting the chamber to the mechanical pump. The valve was controlled by the controller for the pressure guage. The sensors were mounted on the a test head (Figure 5.1). It consists of a copper plate that has a heater mounted on it. The sensor is mounted on a sapphire disc that electrically isolates the sensor from the heater but maintains good thermal contact. The temperature of the substrate is monitored by a thermocouple in contact with the quartz plate. This fixture
Figure 5.1: Schematic of the sensor characterization platform built by SNL at Livermore, Ca.

Figure 5.2: Images of sensor characterization set-up built by SNL for this work.
is mounted on a cylindrical ceramic holder. Contact to the sensor pads is made by pins mounted on a ceramic ring that clamps down on the sensor. The ceramic ring is attached to the ceramic holder. The pins are contacted by connectors running through the ceramic holder. The entire assembly is mounted on an electrical feed through. The feedthrough is connected to the vacuum chamber through a bellow assembly (Figure 5.1). The heater is connected to a power supply that is controlled by the temperature read out for the thermocouple. Chemiresistors are measured using an op-amp circuit (Appendix A). The voltages from the op-amp circuit was input into a computer through a 16 bit A/D PCMCIA card and the data is processed by the computer using a program written in LabView\(^1\). The output voltages from the circuit are proportional to changes in resistance of chemiresistors. These voltages were converted to resistance values by calibrating the circuit to known changes in resistance (dR/R). The voltage change had a linear relation to changes in resistance. The circuits were calibrated for resistances of 500 to 2000 Ω and behaved consistently for the resistors in that range.

5.1.1 Sensor Testing Protocol

After the sensors were mounted on the test head, they were evaluated for electrical continuity. Any defective resistor lines detected were isolated from the circuit. The test head was subsequently mounted on the chamber and pumped down. The sensors were then annealed in an atmosphere of 2% H\(_2\) and 98% Ar gas at 200 torr pressure and 200°C. This annealing process improves the stability of the sensor response [1]. The sensors were tested at temperatures of 75°C, 100°C, 125°C and 150°C and at pressures from 100 to 500 torr, however, most of the testing was performed at 100 torr and 75°C. All the gas mixtures were diluted in Ar. The nominal gas composition used for testing the sensor was 1% H\(_2\) in Ar. The CO/H\(_2\) mixtures consisted of 5% CO, 1% H\(_2\) in Ar. Sensors were also tested in higher concentrations of H\(_2\) (up to 40% H\(_2\) in Ar at 500 torr) and CO (1% H\(_2\), 25% CO in Ar at 100 torr) as well.

5.2 Sensor Response – Effect of Hydrogen

Hydrogen molecules from the gas phase adsorb on the Pd metal surface and dissociate into atoms. In Pd, H\(_2\) preferentially adsorbs on adjacent surface hollow sites\(^2\). The spontaneous

\(^1\)The program was written by Anthony McDaniel and Dennis Morrison, Combustion Research Facility, SNL, Livermore, Ca

\(^2\)The three-fold hollow sites in <111> planes or the four-fold hollow sites in <100> planes in fcc lattice
dissociation of H$_2$ is thought to occur due to interaction of the $\sigma$-bonding orbital of H$_2$ with the d-orbital of Pd atoms [2]. Subsequently, hydrogen atoms diffuse into the metal, occupying orthogonal interstitial sites in the fcc lattice. This two step process is thought to be limited by adsorption and subsequent dissociation of the H$_2$ molecule at the surface. Dissolved hydrogen atoms occupying the interstitial sites in the Pd lattice are thought to cause increased scattering of electrons, manifested by an increase in resistivity of these films [3,4].

Figure 5.3 illustrates the response of a 1000 Å thick, 10 $\mu$m wide and 4000 $\mu$m long Pd metal line ($\sim$1200 Ω resistance) to H$_2$ ambient (1% H$_2$ in Ar gas) at 75°C substrate temperature. The initial linear region of the curve during hydrogenation and dehydrogenation corresponds to a purely diffusion controlled regime. However, it is clear that the response of Pd films to H$_2$ is not solely diffusion controlled, but an alternate process, like dissociation/dissolution at the surface tends to dominate, as indicated by the deviation from linearity of the curve. This is clearly seen during the recovery of the sensor. The sensor recovery is subsequently an exponential decay.

![Figure 5.3](image.png)

Figure 5.3: Sensor (Pd film 1000 Å thick, $\sim$1200 Ω) response to 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature.

### 5.2.1 Geometric Effects

Adsorption being a surface phenomena was thought to be impacted by the surface topology (on a macroscale) of the Pd thin film. To investigate the effect of resistor geometry on H$_2$ adsorption, resistor structures with varying length, width, perimeter to area ratio, edge
to perimeter ratio and active to non-active areas, but same resistance, were tested. These structures were fabricated on a single die and were tested simultaneously (see Appendix B). Figure 5.4 shows the measured responses of some of these structures to 1% H$_2$ at 75°C. From the measured response of these sensors, it is clear that geometry has little effect on sensor response. The small variations in the response of some of the metal lines can be attributed to non-uniformities in the Pd films resulting from fabrication related issues.

5.2.2 Effect of Thin Film Resistance

Adsorption of H$_2$ changes the resistivity of the Pd thin film, hence in principle there should be no change in sensor response (dR/R) for a given partial pressure of H$_2$ ($P_{H_2}$), irrespective of the total resistance of the resistor. This was confirmed by measuring sensor response to H$_2$ using chemiresistors with different resistances. Figure 5.5 shows the measured response of chemiresistors with resistances of 1200 Ω and 2200 Ω. The data shows a higher level of noise and drift in the sensor response resulting in higher dR/R values (~10 - 15%) for 1% H$_2$ in Ar at 100 torr. The small observed variations are attributed to fabrication variations in the sensors (e.g. contact resistance between Pd and Al contact pads, line widths, etc.). Also, 2000 Ω sensor resistance is in the upper limit of the capability of the measuring circuit. This is also thought to be partially responsible for the high level of noise and drift in the data.

Figure 5.4: Response of Pd thin film resistors (1000 Å thick, ~1200 Ω) with different geometries to 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature.
5.2.3 Effect of Hydrogen Partial Pressure

Dissolution of diatomic gases in metal, in general, is governed by Sievert’s law, which states that the amount of gas dissolved (low concentrations) in a metal is proportional to the square root of its partial pressure. Dissolution of \( \text{H}_2 \) in Pd is governed by Seivert’s law as seen by the square root dependence of partial pressure (\( P_{\text{H}_2} \)) to the sensor response (\( (dR/R)_{\text{max}} \)). \( dR/R \) is proportional to the amount of hydrogen dissolved in Pd (\( H_{\text{Me}} \)). Figure 5.6 shows the linear dependence of sensor response (\( (dR/R)_{\text{max}} \)) to \( \sqrt{P_{\text{H}_2}} \). However, it should be noted that there is a slight deviation from Seivert’s law at higher partial pressures of \( \text{H}_2 \).

5.2.4 Effect of Substrate Temperature

The adsorption process is highly sensitive to the substrate temperature as the sticking coefficient of adsorbing gas has a strong temperature dependence. The sticking coefficient data available in the literature for \( \text{H}_2 \) on Pd indicates a strong dependence on temperature [5, 6]. The sticking coefficient drops as the temperature of the substrate increases, thereby reducing the probability of \( \text{H}_2 \) atoms adsorbing on the Pd surface. The measured response of sensors (Figure 5.7) as a function of substrate temperature indicates that there is lowering of the sensitivity of the sensors, seen as a decrease in the \( (dR/R)_{\text{max}} \) value. The data also suggests that the sensor’s response is slower at higher temperatures as fewer atoms adsorb on the Pd surface because of the lowering of the sticking coefficient. This is indicated by
Figure 5.6: Sensor (Pd film 1000 Å thick, \( \sim 1200 \, \Omega \)) response to \( \text{H}_2 \) concentrations (1\%, 2\%, 10\%, 15\% 25\% and 35\%) in Ar at 500 torr pressure and 75\°C sensor temperature.

Figure 5.7: Substrate temperature dependence of sensor (Pd film 1000 Å thick, \( \sim 1200 \, \Omega \)) response to 1\% \( \text{H}_2 \) in Ar at 100 torr.

the shallower slopes for the adsorption and desorption parts of the curve. The data for sensor response at 125\°C has significant drift and shows sensitivity to \( \text{H}_2 \) that is equal to its sensitivity at 100\°C (Figure 5.7). This could be due to the fact that the sticking coefficient of \( \text{H}_2 \) on Pd drops sharply in the temperature range of 50\°C to 100\°C but, drops more gradually at higher temperatures. Hence, the sensor has very similar sensitivity at 100\°C and 125\°C.

The vapor-solid phase equilibrium is governed by the Clausius-Clapeyron equation. Here,
the dissolution of \( H_2 \) in Pd is a reversible equilibrium reaction. The \((dR/R)_{\text{max}}\) for Pd films as a function of temperature has an exponential dependence to the inverse of temperature of the substrate. Since \((dR/R)_{\text{max}}\) is proportional to the square root of partial pressure (Seivert’s law), \( \ln(P_{H_2}) \) is proportional to inverse of the substrate temperature. This is

\[
\ln(\sqrt{P_{H_2}}) = \ln \left( K \cdot \frac{n}{1-n} \right) ; \quad n = \frac{H}{P_{d}} ; \quad K = \exp \left[ \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{2R} \right]
\]

where \( \Delta S^\circ \) is the change in entropy of adsorption and \( R \) the gas constant.

### 5.3 Sensor Response – Effect of Gas Mixtures

Gas molecules like \( H_2, CO, C_2H_2, SO_2 \) and \( H_2S \), to name a few, have a strong propensity to adsorb on the surface of Pd. These gas molecules compete for surface sites on Pd. Sulphur

Figure 5.8: Substrate temperature dependence of sensor (Pd film 1000 Å thick, \( \sim 1200 \text{ \textOmega} \)) response \( ((dR/R)_{\text{max}}) \) to 1% \( H_2 \) in Ar at 100 torr. Clearly seen in the plot (Figure 5.8) between \( dR/R \) (log scale) and \( 1/T \). The slope of the plot is proportional to the enthalpy of adsorption of \( H_2 \) on the Pd surface.

Sensor response as function of hydrogen partial pressure at different substrate temperatures (Figure 5.9) indicates that the slope of the line changes. This is consistent with Seivert’s law as the constant of proportionality in Seivert’s law is a function of enthalpy of adsorption (\( \Delta H \)) and the temperature (\( T \)).
containing gases chemically react with Pd and leave behind sulphur deposits on the surface, thus poisoning the metal surface. The process is usually irreversible and particularly acute with H$_2$S gas. In the case of CO, the gas molecule physically adsorbs on the metal surface, preventing H$_2$ from adsorbing on those sites [7]. This process is reversible and is temperature dependent (sticking coefficient is strongly dependent on temperature of the surface [8]).

5.3.1 Response to CO and H$_2$

CO adsorbs on top, bridge or hollow sites in fcc and bcc lattice. Energetically these sites are very similar, hence CO will adsorb in all these sites at higher concentrations. Data available in the literature indicates that CO starts to adsorb on the hollow sites in the Pd lattice at low concentrations (< 0.1 mono-layer) and subsequently on bridge and top sites at progressively higher concentrations [9–13]. The initial sticking coefficient of CO on Pd is ~1 (compared to 0.5 to 0.7 for H$_2$) at temperatures below 125K [5,6], indicating that it would adsorb on the Pd metal surface (physical adsorption) more effectively than H$_2$. At higher temperatures, the sticking coefficients are substantially lower for both CO and H$_2$. Exposure of Pd surfaces to gas mixtures containing both H$_2$ and CO, results in a sluggish response, as seen in Figure 5.10.

From the response of chemiresistors to CO and H$_2$ gas mixtures, it is clear that there is no attenuation of the resistance change, indicating that H$_2$ adsorbs and diffuses into the Pd lattice despite CO occupying adsorption sites on the Pd surface (larger sticking...
coefficient of CO). This is counter to the data in the literature [14, 15], that indicates that CO attenuates the sensor response (MOS based sensor). However, this disagreement could be due to differences in the mechanism of operation of the MOS based hydrogen sensors (with Pd gate). Measurements (LEEDS, STM, etc) made on adsorption of CO on single crystal Pd surfaces [9, 10, 12, 13] indicates that at low CO concentrations, CO molecules adsorb on the surface sites in ordered structures and do not occupy all the hollow sites. Hence, there are sufficient hollow sites for H$_2$ to adsorb on. This could possibly explain the lack of attenuation, but, sluggish response of the sensors to CO, H$_2$ gas mixtures. When CO is cycled with H$_2$ (sensor exposed to 1% H$_2$ initially and 5% CO is cycled, keeping the H$_2$ flow constant), there is no noticeable change in the ∆R values (see Figure 5.11). This suggests that at these concentration of CO, it does not displace adsorbed H$_2$ on the surface.

At higher temperatures the sticking probability of CO on Pd drops. This reduction of sticking coefficient leads to reduced adsorption of CO on Pd, increasing the efficiency of dissolution of H$_2$ in Pd. However, as indicated earlier, the sticking coefficient of H$_2$ decreases at higher temperature as well, resulting in fewer molecules of H$_2$ adsorbing on the Pd surface. The combination of these two processes leads to a reduction of sensitivity of the sensor, but a speedier response in the presence of CO. This is clearly seen in the response of sensors at 125°C (see Figure 5.12). However, there is substantial drift in the sensor response that causes the baseline response of the sensor to continuously drift at this temperature. It is thought that annealing the thin films at 300°C to 400°C and improvements in processing steps would eliminate the drift possibly due to passivation of defects in the thin film [16].

Figure 5.10: Sensor (Pd film 1000 Å thick, ∼1200 Ω) response to 5% CO and 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature.
5.3.2 Effect of SO$_2$

Sulphur containing gases, like SO$_2$ and H$_2$S poison catalytic metals like Pd due to formation of sulphur deposits on the metal surface. H$_2$S has been known to adsorb and dissociate on Pd surface, leaving behind sulphur, thus blocking surface sites. This is an irreversible change and results in attenuation of the sensor response to H$_2$. Compared to H$_2$S, SO$_2$ is less effective in poisoning the Pd metal surface. Exposing Pd chemiresistors to SO$_2$ at elevated temperatures for extended periods of time (∼16 hrs) leads to an attenuation of the
sensor response as observed in Figure 5.13. The observed attenuation was irreversible.

![Graph showing sensor response to SO$_2$ exposure](image)

Figure 5.13: Sensor (Pd film 1000 Å thick, $\sim$1200 Ω) response to 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature after 16 hour exposure to SO$_2$ at 100 psi pressure and 100°C gas temperature.

### 5.4 Sensor Response – Thin Film Morphology

Adsorption of hydrogen on Pd, being a surface phenomenon is affected by the surface morphology of the film. By sputtering Pd films at different pressures (5 and 25 mtorr), films of different morphology were grown. Predictably, these films had a different response to H$_2$. Figure 5.14 shows a comparison of the response of these two films when exposed to hydrogen. As seen in Figures 4.2, 4.6, the films deposited at 5 mtorr have a dense and relatively smooth texture when compared to films deposited at 25 mtorr. The film with smooth texture has a rapid response to H$_2$. However, films with rougher texture (more defects, higher resistance) had a slower response and diminished sensitivity to H$_2$.

Films deposited at 25 mtorr have a larger surface area (increased surface roughness, as seen in AFM images) and prominent grain boundaries. Hence incorporation of hydrogen in Pd could be thought to occur through two path ways, namely surface sites and diffusion through grain boundaries. One would expect the latter path to have a slower response owing to diffusion of Pd through the grain boundary. The presence of a larger, prominent grain boundary increases the overall resistivity and hence the resistance of the films due to increased scattering at the grain boundaries. In the films tested here, the resistance increased from 1200 Ω to 2200 Ω. However, in these films, change in resistance (dR) as a
result of H₂ adsorption does not increase substantially from the 5 mtorr films (same volume of material – area and thickness of the film) as it is solely dependent on the solubility of hydrogen in Pd. Hence, dR/R for this film is lower than dR/R for the films deposited at 5 mtorr (denser films) as seen in the reduced sensitivity to H₂ (Figure 5.14).

The effect of morphology is more prominent in the response of these sensors to CO and H₂ gas mixtures. Figure 5.15 indicates that morphology improves the response (less sluggish) of the sensor in presence of CO when compared to sensors made from dense/smooth Pd films. It is thought that the morphology (columnar structure with grain boundaries, <1 nm) causes the film to act like a sieve, separating the larger CO molecule from the smaller H₂ molecule due to the difference in their diffusivities (limited by atomic size). Hence, CO molecules are slower in reaching the sites in the grain boundaries, thus making those sites more readily available for adsorption of H₂. Hence, compensating for the lose of surface sites (top surface of the film) occupied by CO. This mechanism could possibly explain the improvement in sensor response for CO - H₂ gas mixtures.

### 5.5 Circuit Model for Temporal Response of Sensors

The temporal response of the films with greater morphology (rough surface texture and increased grain boundaries) could be understood by modelling the two pathways of H₂ transport into Pd (as described above) through a combination of series and parallel capacitances.
Figure 5.15: Sensor (Pd film deposited at 25 mtorr - rough texture, 1000 Å thick, \(~\sim 2100 \) Ω) response to 5% CO and 1% H₂ in Ar at 100 torr pressure and 75°C sensor temperature. The model has the following assumptions and constraints.

1. The voltage \(v\) across the circuit represents hydrogen partial pressure, which is assumed to remain constant (at constant \(P_{H_2}\)).

2. The current \(i(t)\) in the circuit represents the temporal response of the sensor.

3. Each resistor element \(r\) in the circuit represents the contribution of a particular pathway for H₂ transport into and out of Pd (adsorption/desorption).

4. Capacitor \(C_{Pd}\) represents the solubility of H₂ in Pd.

5. For better comparison of the temporal evolution of currents in different circuits, the currents were normalized by dividing the transient current with the steady state current of the circuit.

\[
i_i(t) = \frac{i(t)}{v/r_{eff}}; \quad i = 1, 2, 3, \ldots
\]

where \(r_{eff}\) = effective resistance of the circuit, \(v\) = voltage drop in the circuit

This model does not explain the variations in the sensitivity of the sensors as only the transport of H₂ into and out of Pd is taken into account here.
**RC Circuit**

In a circuit consisting of a resistor \((r_{eff})\) and capacitor \((C)\) in parallel (Figure 5.16), the temporal evolution of current during the charging and discharging of the capacitor is given by the following equations.

\[
i(t) = 1 - \exp\left(-\frac{t}{r_{eff}C}\right)
\]

\[(5.1)\]

The circuit reaches steady state when the capacitor is completely charged. At steady state, a constant current flows through the resistor elements in the circuit. This is analogous to the establishment of equilibrium between the adsorption/desorption process on Pd surface and the solubility of H\(_2\) in Pd. When the power supply to the circuit is turned off, the capacitor tries to maintain the current in the circuit by supplying the circuit with the stored charge, in the process discharging itself. The normalized current in the circuit during the discharging of the capacitor is given by the following equation.

\[
i(t) = \exp\left(-\frac{t}{r_{eff}C}\right)
\]

\[(5.2)\]

The temporal evolution of current in this circuit has a shape similar to the response of Pd chemiresistor to H\(_2\) (Figure 5.17). From equations 5.1 and 5.2 it is clear that an increase in the total resistance or capacitance of the circuit would slow its current response. This is analogous to the slowing of the sensor response in the presence of gas mixtures containing H\(_2\), like CO and H\(_2\).
5.5.1 Case 1: Model for Adsorption of H\(_2\) in Pd (5 mtorr film)

For a given partial pressure (\(P_{H_2}\)) of hydrogen and fixed temperature, the temporal response of Pd thin film resistor can be represented by a circuit (Figure 5.18) consisting of a resistor (\(r_{H_2}\)) and a capacitor (\(C_{Pd}\)). The resistor (\(r_{H_2}\)) represents the adsorption/desorption of H\(_2\) on Pd surface and the subsequent transport of adsorbed H\(_2\) into and out of Pd lattice. The capacitor (\(C_{Pd}\)) represents the dissolution of H\(_2\) in Pd. The current (\(i_1(t)\)) represents the temporal response of the sensor to hydrogen adsorption/desorption process.

\[
\begin{align*}
    i_1(t) &= 1 - \exp\left(-\frac{t}{r_{H_2}C_{Pd}}\right) \quad \text{adsorption} \\
    i_1(t) &= \exp\left(-\frac{t}{r_{H_2}C_{Pd}}\right) \quad \text{desorption}
\end{align*}
\]

Figure 5.18: Circuit representing the temporal response of sensor (Pd film deposited at 5 mtorr - smooth texture, 1000 Å thick, \(\sim\)1200 Ω) response to 1% H\(_2\) in Ar at 100 torr pressure and 75°C sensor temperature.
From this equation it is clear that a change in the total resistance of the circuit will change the temporal evolution of \( i_1 \), as is the case when Pf film is exposed to gas mixtures containing \( \text{H}_2 \) and CO.

### 5.5.2 Case 2: Model for Adsorption of \( \text{H}_2 \) and CO in Pd (5 mtorr film)

The influence of CO is modeled by adding a resistance \( (r_{CO}) \) in series with \( r_{H_2} \) (Figure 5.19). This represents additional hinderance for \( \text{H}_2 \) to adsorb on Pd surface, as is the case with CO, which, blocks adsorption site on Pd surface by occupying it. Hence, \( \text{H}_2 \) has to diffuse through partially CO covered surfaces to find surface sites. The increased resistance in the circuit decreases the rate of charging of the capacitor and hence the rate of increase in the current flowing through the circuit. The current \( (i_2(t)) \) representing the temporal response of the sensor would be given by the following equation.

\[
\begin{align*}
    i_2(t) &= 1 - \exp\left(-\frac{t}{r_{eff}C_{Pd}}\right) \quad \text{(adsorption)} \quad (5.5) \\
    i_2(t) &= \exp\left(-\frac{t}{r_{eff}C_{Pd}}\right) \quad \text{(desorption)} \quad (5.6)
\end{align*}
\]

where

\[
    r_{eff} = r_{H_2} + r_{CO}
\]

The rate of change of \( i_2(t) \) is less than rate of change in \( i_1(t) \), due to additional resistor in this circuit, representing the effect of CO and hence, the sluggish response to \( \text{H}_2 \) in presence of CO.
5.5.3 Case 3: Model for Adsorption of H\textsubscript{2} in Pd (25 mtorr film)

The Pd films deposited at 25 mtorr has a rough surface texture and prominent grain boundaries. It is composed of distinct columns separated by an interface (Figure 4.6). It was proposed the there are two path ways for diffusion of hydrogen into the Pd lattice, namely, the top surface of Pd and along the grain boundary of the Pd columns. The former pathway is represented by the resistor ($r_{H_2}$) and capacitor ($C_{Pd}$) in parallel. The latter pathway is a two step process: diffusion through the grain boundary to a site on columnar Pd grain followed by adsorption/desorption on surface of the grain. This pathway is represented by two resistors in series, $r_{GB}$ representing the grain boundary diffusion of H\textsubscript{2} and $r_{H_2}$ representing the adsorption/desorption of H\textsubscript{2}. For simplicity, the sites on the grain boundary are assumed to be identical to the top surface of the grains. The dissolved H\textsubscript{2} in Pd due to this process is represented by a capacitor ($C_{Pd}$) in parallel with the resistors ($r_{H_2}$ and $r_{GB}$) in series. These two pathways represent parallel processes for H\textsubscript{2} adsorption/desorption in Pd thin film and hence represented by a parallel circuit (Figure 5.20). The second capacitor ($C_{pd}$) represents the dissolution of H\textsubscript{2} in Pd adsorbed on the grain boundary sites.

![Circuit representing the temporal response of sensor (Pd film deposited at 25 mtorr - smooth texture, 1000 Å thick, ∼2200 Ω) response to 1% H\textsubscript{2} in Ar at 100 torr pressure and 75°C sensor temperature.](image)

Figure 5.20: Circuit representing the temporal response of sensor (Pd film deposited at 25 mtorr - smooth texture, 1000 Å thick, ∼2200 Ω) response to 1% H\textsubscript{2} in Ar at 100 torr pressure and 75°C sensor temperature.

The grain boundary adsorption of H\textsubscript{2} is limited by the diffusion rate of H\textsubscript{2} through the grain boundary. This limitation is not present for the top surface of Pd. Hence, these films will have a more sluggish response when compared to the denser films (5 mtorr films). This is clearly seen in the slower saturation and decay rates of the current in the circuit representing the temporal response of 25 mtorr Pd films (equations 5.7 and 5.8) due to a higher $r_{eff}C_{eff}$. 

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value in this circuit.

\[ i_3(t) = 1 - \exp \left( -\frac{t}{r_{eff}C_{eff}} \right) \] (adsorption) (5.7)

\[ i_3(t) = \exp \left( -\frac{t}{r_{eff}C_{eff}} \right) \] (desorption) (5.8)

where

\[ r_{eff} = \frac{r_{H_2}(r_{H_2} + r_{GB})}{2r_{H_2} + r_{GB}} \]

\[ C_{eff} = 2C_{Pd} \]

The slower saturation/decay of the current in this circuit (compared to \( i_1(t) \)) is due to the higher “re” value \( r_{eff}C_{eff} \) of this circuit (see Figure 5.17), as seen below.

\[ r_{eff}C_{eff}|_{5 \text{ mtorr}} = r_{H_2} \cdot C_{Pd} \]

\[ r_{eff}C_{eff}|_{25 \text{ mtorr}} = \frac{r_{H_2}(r_{H_2} + r_{GB})}{2r_{H_2} + r_{GB}} \cdot 2C_{Pd} \]

\[ \frac{\frac{r_{H_2}(r_{H_2} + r_{GB})}{2r_{H_2} + r_{GB}} \cdot 2C_{Pd}}{\frac{2(r_{H_2} + r_{GB})}{2r_{H_2} + r_{GB}}} \leq \frac{2}{1 + \frac{r_{H_2}}{r_{H_2} + r_{GB}}} \leq 1 \]

\[ \therefore \frac{2}{1 + \frac{r_{H_2}}{r_{H_2} + r_{GB}}} \geq 1 \]

\[ \therefore r_{eff}C_{eff}|_{25 \text{ mtorr}} \geq r_{eff}C_{eff}|_{5 \text{ mtorr}} \]

### 5.5.4 Case 4: Model for Adsorption of H\(_2\) and CO in Pd (25 mtorr film)

Presence of CO on the Pd surface limits the surface sites available for H\(_2\) to adsorb. This additional hurdle is accounted for by the inclusion of a resistor \( r_{CO} \) in series with \( r_{H_2} \), representing the additional resistance for transport of H\(_2\) to the surface sites (top surface) on Pd (Figure 5.21). This circuit representation was chosen because, CO, being a larger molecule would not be able to diffuse along the grain boundary as efficiently as H\(_2\). Hence, its effect on the grain boundary component \( (r_{GB} + r_{H_2}) \) is negligible. Therefore, the circuit could be represented by two pair of series resistors \( (r_{GB} + r_{H_2}) \) and \( r_{H_2} + r_{CO} \) in parallel
with each other (Figure 5.21). The two capacitors \((C_{Pd})\) represent the solubility of \(H_2\) in Pd due to the two pathways. The rate of change in current \((i_4)\) flowing in this circuit would

\[
\begin{align*}
    i_4(t) &= 1 - \exp\left(-\frac{t}{r_{eff}C_{eff}}\right) \quad \text{(adsorption)} \tag{5.9} \\
    i_4(t) &= \exp\left(-\frac{t}{r_{eff}C_{eff}}\right) \quad \text{(desorption)} \tag{5.10}
\end{align*}
\]

where

\[
\begin{align*}
    r_{eff} &= \frac{(r_{H2} + r_{CO})(r_{H2} + r_{GB})}{2r_{H2} + r_{GB} + r_{CO}} \\
    C_{eff} &= \frac{2r_{H2} + r_{GB}}{2C_{Pd}}
\end{align*}
\]

Addition of \(r_{CO}\) increases the effective resistance of the circuit and hence increases the “rc” value \((r_{eff}C_{eff})\) of this circuit (see Figure 5.17), implying that the response would be slower in presence of CO, as shown below.

\[
\begin{align*}
    r_{eff}\big|_{H2} &= \frac{r_{H2}(r_{H2} + r_{GB})}{2r_{H2} + r_{GB}} \\
    r_{eff}\big|_{H2+CO} &= \frac{(r_{H2} + r_{CO})(r_{H2} + r_{GB})}{2r_{H2} + r_{GB} + r_{CO}} \\
    \frac{r_{H2}(r_{H2} + r_{GB})}{2r_{H2} + r_{GB}} &= \frac{(r_{H2} + r_{CO})(r_{H2} + r_{GB})}{2r_{H2} + r_{GB} + r_{CO}} \\
    \therefore \frac{r_{H2}}{2r_{H2} + r_{GB}} &= \frac{r_{H2} + r_{CO}}{2r_{H2} + r_{GB} + r_{CO}}
\end{align*}
\]
dividing both the sides of the equation by \( \frac{r_{H_2}}{2r_{H_2} + r_{GB}} \) we get

\[
\frac{1}{1 + \frac{r_{CO}}{r_{H_2}}} \geq \frac{1}{1 + \frac{r_{CO}}{2r_{H_2} + r_{GB}}}
\]

here \( \frac{r_{CO}}{r_{H_2}} \geq \frac{r_{CO}}{2r_{H_2} + r_{GB}} \)

\[
\therefore 1 \leq \frac{1}{1 + \frac{r_{CO}}{r_{H_2}}}
\]

\[
\therefore r_{eff}|_{H_2} \leq r_{eff}|_{H_2+CO}
\]

A comparison of the ratios of \( r_{eff}C_{eff} \) with CO and \( H_2 \) gas mixture and \( H_2 \) gas for the 5 mtorr and 25 mtorr Pd film indicates that the ratio is larger for the 5 mtorr film.

\[
\frac{r_{eff}C_{eff}|_{H_2+CO}}{r_{eff}C_{eff}|_{H_2}} \Bigg|_{Pd, \ 5 \ mtorr} = \frac{(r_{H_2} + r_{CO})C_{Pd}}{r_{H_2}C_{Pd}}
\]

\[
= \frac{r_{H_2} + r_{CO}}{r_{H_2}}
\]

\[
\frac{r_{eff}C_{eff}|_{H_2+CO}}{r_{eff}C_{eff}|_{H_2}} \Bigg|_{Pd, \ 25 \ mtorr} = \frac{(r_{H_2} + r_{CO})(r_{H_2} + r_{GB})2C_{Pd}}{2r_{H_2}r_{H_2}r_{H_2} + r_{GB}r_{CO}}
\]

\[
= \frac{r_{H_2} + r_{CO}}{1 + \frac{r_{CO}}{2r_{H_2} + r_{GB}}}
\]

\[
\therefore \frac{r_{eff}C_{eff}|_{H_2+CO}}{r_{eff}C_{eff}|_{H_2}} \Bigg|_{Pd, \ 5 \ mtorr} \geq \frac{r_{eff}C_{eff}|_{H_2+CO}}{r_{eff}C_{eff}|_{H_2}} \Bigg|_{Pd, \ 25 \ mtorr}
\]

This suggests that the 5 mtorr Pd film is more severely affected by CO when compared to the 25 mtorr as suggested by the data for Pd thin film resistors deposited at 25 mtorr pressure.

A semi-log plot of the sensor response during the desorption process (after \( H_2 \) and CO + \( H_2 \) gas flow is stopped) indicates that the thin films have an almost linear behavior (Figure 5.22). This suggests that the response follows an exponential decay similar to the current decay in an RC circuit. By assuming the slopes of the lines to be proportional to \( 1/r_{eff}C_{eff} \) the conclusions drawn by the circuit model are clearly seen. Hence, it can be concluded that the circuit model is a reasonable qualitative description of the processes responsible for the response of the thin films to \( H_2 \) and CO and \( H_2 \) gas mixture.
Figure 5.22: The normalized sensor response \( ((dR/R)/(dR/R)_{\text{max}}) \) as a function of time during the desorption process (H\(_2\) and CO + H\(_2\) flow stopped) for Pd film deposited at 5 mtorr (1000 Å thick and \( \sim 1000 \) Ω and 25 mtorr (1000 Å thick, \( \sim 2200 \) Ω). The data was collected at 100 torr pressure and sensor temperature was maintained at 75°C.

5.6 Semi-permeable Coatings – Silicon Dioxide

Oxides of silicon (silica, thermally grown SiO\(_2\), silica glass) have long been known to be permeable to H\(_2\) [17–20]. The permeability of H\(_2\) in SiO\(_2\) has been attributed to its structure. Granular random network model is has been widely used to describe the structure of amorphous SiO\(_2\). In this model, the amorphous phase is thought to consist of quasi-crystalline structures of about 3 nm diameter, linked at their boundaries through strained interfaces [21,22]. Molecular dynamics studies of molecular diffusion of hydrogen through SiO\(_2\) indicate that the transport of H\(_2\) in SiO\(_2\) consists of “jumps” through the network and “trapping” of some of the molecules [23] by the network. This is akin to the flow of water through a cotton sponge, which retains some water while allowing the excess to flow through.

5.6.1 Sensor Response – Effect of Hydrogen

Measurements made on fused quartz (SiO\(_2\)) by Lee et al [18] indicates that transport of H\(_2\) through SiO\(_2\) is not a purely diffusive process, but diffusion moderated by solubility of H\(_2\) in SiO\(_2\). The permeability data for H\(_2\) through quartz shows a profile very similar to the response of Pd to H\(_2\), however, the time for attaining steady state is much longer and dependent on thickness of the quartz membrane. Hence, in Pd sensors covered with SiO\(_2\)
films, the lag in response is due to the diffusion of $H_2$ through oxide.

Measurements on SiO$_2$ coated chemiresistors (see Figure 5.23) indicates that there is a delay in response to $H_2$. This is attributed to the transport of $H_2$ through the oxide by a combination of diffusion and dissolution process. However, the observed change in steady state resistance ($dR$) of these chemiresistors is larger than those chemiresistors that do not have the SiO$_2$ coating, when exposed to similar concentrations of hydrogen. This could be attributed to the trapping of hydrogen within Pd film and the presence of dissolved $H_2$ in SiO$_2$, that could act as an additional source of $H_2$. This could also explain the observed drift in these sensors. The recovery of these sensors (coated with SiO$_2$) is decelerated as well, indicating that similar mechanisms govern the transport of $H_2$ through the oxide, both from the ambient to the Pd surface and viceversa. In this case, $H_2$ formed by recombination of $H_{ad}$ at the Pd surface, had to diffuse through the oxide and back to the top surface of the oxide.

A schematic of the cross-section of Pd/SiO$_2$ stack (Figure 5.24) indicates that the side walls of the metal lines are not covered with SiO$_2$. This was due to the process used in fabrication of these sensors. Thus the adsorbing gases would see Pd surface on the side walls, an alternate pathway for $H_2$. The response to $H_2$ is a result of these two pathways. However, it should be noted that the surface area represented by the side wall is substantially smaller than the top surface area. For a 10 $\mu$m wide and 1000 Å thick line the ratio of top surface area by the side wall area is 50 to 1.

Figure 5.23: Effect of SiO$_2$ thickness (200 Å, 400 Å and 800 Å) on sensor (Pd film 1000 Å thick, ~1200 Ω) response to 1% $H_2$ in Ar at 100 torr pressure and 75°C sensor temperature.
5.6.2 Effect of SiO$_2$ Film Thickness

Data for sensor response as a function of SiO$_2$ film thickness indicates that the permeation of H$_2$ declines considerably as the thickness is increased from 400 to 800 Å (Figure 5.25). The thickness dependence is non-linear indicating a non-trivial mechanism for H$_2$ response. The uncovered side walls of the metal lines is also an issue that complicates the interpretation of the effect of thickness. The rate of response of these sensors has an exponential relation to the inverse of the substrate thickness (Figure 5.26). However, it must be pointed out that these experiments were not designed for acquiring transient data, hence the rates indicated are not accurate as no allowance has been made to eliminate the transient effects of the changes in gas composition in the test chamber. The diffusion equation derived by Lee et al [18] does have an exponential relation to the oxide film thickness, for a first order approximation. However, this data includes the additional effect of H$_2$ adsorption and dissolution in Pd.

5.6.3 Effect of Substrate Temperature

The data for sensor response as a function of temperature for different thickness of oxide shows an exponential relation (Figure 5.27). This is very similar to the response of Pd films (without barrier layer) to H$_2$ as a function of temperature (Figure 5.8). However, the spread in the data is less than an order of magnitude, hence cannot be accurately fitted to an exponential relation. The data for the response rate decays exponentially with the inverse of temperature (Figure 5.28). Again, the range of data covers less than an order of magnitude and hence cannot be accurately fitted to a exponential relation. However, this kind of dependence does indicate that some form of diffusion process is in play in the sensor response.
Figure 5.25: Effect of SiO₂ thickness (200 Å, 400 Å and 800 Å) on sensor (Pd film 1000 Å thick, ~1200 Ω) sensitivity to 1% H₂ in Ar at 100 torr pressure and 75°C sensor temperature.

Figure 5.26: Effect of SiO₂ thickness (200 Å, 400 Å and 800 Å) on sensor (Pd film 1000 Å thick, ~1200 Ω) response rate to 1% H₂ in Ar at 100 torr pressure and 75°C sensor temperature.
Figure 5.27: Effect of substrate temperature on sensor (400 Å and 800 Å SiO$_2$ film, Pd film 1000 Å thick, $\sim$1200 Ω) sensitivity to 1% H$_2$ in Ar at 100 torr pressure.

Figure 5.28: Effect of substrate temperature on sensor (800 Å SiO$_2$ film, Pd film 1000 Å thick, $\sim$1200 Ω) response rate to 1% H$_2$ in Ar at 100 torr pressure.
5.6.4 Effect of H₂ Partial Pressure

The data for sensors with oxide films display good agreement with Sievert’s law as seen by the linear dependence of sensor response to square root of H₂ partial pressure (Figure 5.29). The data for 200 Å oxide was anomalous due to possible contamination with SiC during thin film deposition. The data for different thickness are nearly parallel indicating that the surface characteristics remain unchanged with barrier film thickness (the slope of the straight line is proportional to the enthalpy of adsorption of H₂ on Pd).

![Figure 5.29: SiO₂ covered (200 Å, 400 Å and 800 Å thick) sensor (Pd film 1000 Å thick, ~1200 Ω) response to H₂ concentrations (1%, 2%, 10%, rest Ar) at 500 torr pressure and 75°C sensor temperature.](image)

5.6.5 Sensor Response – Effect of Hydrogen and CO

Diffusivity data [17, 24] for gas molecules in SiO₂ indicates that difusivity of diatomic molecules like O₂ are about 5 to 6 orders of magnitude lower than that of H₂, thus SiO₂ films would act like sieves for separating H₂ from gases of larger molecular radii (radii of CO ≈ 1.15Å, radius of H₂ ≈ 0.7Å). Here, sputter deposited oxide films have been used to prevent CO from adsorbing on Pd surface. Data for sensor response (SiO₂ films covering the top surface of the metal line) in presence of CO and H₂ (Figure 5.30) does indicate some improvement in sensor performance, however, the sluggishness of the response still persists. The exact reason for the drift in these sensors is not clear, however, it could partly be due

---

3 Problems with the mass flow controller resulted in variation in the oxygen flow rate during the deposition process.
Figure 5.30: Effect of SiO$_2$ thickness (200 Å, 400 Å and 800 Å) on sensor (Pd film 1000 Å thick, ∼1200 Ω) response to 5% CO and 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature.

to the fact that CO and H$_2$ can adsorb on the uncovered sidewalls of the metal lines, acting as an alternate pathway for adsorption and desorption.

5.6.6 Capacitor-Resistor Circuit Model for Sensor Response

The SiO$_2$ covered Pd film is modelled using a circuit consisting of resistors and capacitors in parallel (Figure 5.31). The effect of SiO$_2$ film on H$_2$ transport to Pd surface is represented by a resistor ($r_{SiO_2}$). The capacitor ($C_{SiO_2}$) represents the solubility of H$_2$ in SiO$_2$. SiO$_2$ film covers the top surface of the Pd metal lines only, hence, the uncovered sidewall acts as an alternate pathway for H$_2$ transport into Pd. This effect is accounted for by adding a resistor ($r_{side,H_2}$) in parallel to the resistors and capacitors representing the transport of H$_2$ through the top surface. It should be noted that, no effort has been made to compare this model with the circuit model for Pd films not covered with SiO$_2$ as it is not possible to compare the magnitudes of $r_{SiO_2}$ and $C_{SiO_2}$ with $r_{H_2}$ and $C_{Pd}$.

Response to H$_2$

The diffusion limited transport of H$_2$ through SiO$_2$ is represented by a resistor ($r_{SiO_2}$) that is in series with the resistor representing the adsorption/desorption of H$_2$ on Pd surface. The solubility of H$_2$ in SiO$_2$ is accounted by a capacitor ($C_{SiO_2}$) connected in parallel with
The solubility of H$_2$ in Pd is represented by a capacitor ($C_{pd}$) connected in parallel with the whole circuit (Figure 5.31). The uncovered side wall provides an alternate pathway for H$_2$ and is represented by a resistor ($r_{side,H_2}$) connected in parallel with $r_{H_2}$ and $r_{SiO_2}$.

Figure 5.31: Circuit representing the temporal response of sensor (Pd film, 1000 Å thick, ∼1200 Ω, SiO$_2$ barrier layer) response to 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature.

The rate of change in current ($i_{1, SiO_2}$) flowing in this circuit would represent the temporal sensor response and is given by equations 5.11 and 5.12.

\[
i_{1, SiO_2}(t) = 1 - \exp \left( -\frac{t}{r_{eff}C_{eff}} \right) \quad \text{(adsorption)} \quad (5.11)
\]

\[
i_{1, SiO_2}(t) = \exp \left( -\frac{t}{r_{eff}C_{eff}} \right) \quad \text{(desorption)} \quad (5.12)
\]

where

\[
r_{eff} = \frac{(r_{H_2} + r_{SiO_2})r_{side,H_2}}{r_{H_2} + r_{SiO_2} + r_{side,H_2}}
\]

\[
C_{eff} = C_{pd} + C_{SiO_2}
\]

**Response to CO and H$_2$**

In presence of CO and H$_2$, the effect of CO is represented by a resistor ($r_{CO}$) in series with $r_{side,H_2}$, representing the side wall that is not covered by SiO$_2$ (Figure 5.32). The diffusivity of CO in SiO$_2$ is very small when compared to that of H$_2$, hence CO molecules will not diffuse through the barrier to Pd top surface, hence its effect is restricted to the exposed
Figure 5.32: Circuit representing the response of sensor (Pd film, 1000 Å thick, ∼1200 Ω, SiO₂ barrier layer) response to 1% H₂, 5% CO, in Ar at 100 torr pressure and 75°C sensor temperature.

\[
i_{2,\text{SiO}_2}(t) = 1 - \exp\left(-\frac{t}{r_{\text{eff}}C_{\text{eff}}}\right) \quad \text{(adsorption)} \quad (5.13)
\]

\[
i_{2,\text{SiO}_2}(t) = \exp\left(-\frac{t}{r_{\text{eff}}C_{\text{eff}}}\right) \quad \text{(desorption)} \quad (5.14)
\]

where

\[
r_{\text{eff}} = \frac{(r_{H_2} + r_{\text{SiO}_2})(r_{\text{side},H_2} + r_{\text{CO}})}{r_{H_2} + r_{\text{SiO}_2} + r_{\text{side},H_2} + r_{\text{CO}}}
\]
\[
C_{\text{eff}} = C_{\text{Pd}} + C_{\text{SiO}_2}
\]

The inclusion of resistance to represent the effect of CO results in an increase in the effective resistance \((r_{\text{eff}})\) of the circuit and hence the “rc” value. This slows the current saturation and decay rates (Figure 5.17), as show below.

\[
\left| r_{\text{eff}} \right|_{H_2} = \frac{(r_{H_2} + r_{\text{SiO}_2})r_{\text{side},H_2}}{r_{H_2} + r_{\text{SiO}_2} + r_{\text{side},H_2}}
\]
\[
\left| r_{\text{eff}} \right|_{H_2+CO} = \frac{(r_{H_2} + r_{\text{SiO}_2})(r_{\text{side},H_2} + r_{\text{CO}})}{r_{H_2} + r_{\text{SiO}_2} + r_{\text{side},H_2} + r_{\text{CO}}}
\]
\[
\left| \frac{(r_{H_2} + r_{\text{SiO}_2})r_{\text{side},H_2}}{r_{H_2} + r_{\text{SiO}_2} + r_{\text{side},H_2}} \right|_{A/V} = \left| \frac{(r_{H_2} + r_{\text{SiO}_2})(r_{\text{side},H_2} + r_{\text{CO}})}{r_{H_2} + r_{\text{SiO}_2} + r_{\text{side},H_2} + r_{\text{CO}}} \right|_{A/V}
\]
Dividing the equation by \( \frac{(r_{H_2} + r_{SiO_2}) r_{side,H_2}}{r_{H_2} + r_{SiO_2} + r_{side,H_2}} \), we get

\[
\frac{r_{side,H_2} + r_{CO}}{r_{side,H_2}} \quad \text{and} \quad \frac{r_{CO}}{1 + \frac{r_{CO}}{(r_{H_2} + r_{SiO_2} + r_{side,H_2})}}
\]

but \( r_{side,H_2} \leq r_{H_2} + r_{SiO_2} + r_{side,H_2} \)

\[
\therefore \quad \frac{1 + \frac{r_{CO}}{r_{side,H_2}}}{\frac{1}{r_{CO}} + \frac{1}{r_{H_2} + r_{SiO_2} + r_{side,H_2}}} \geq 1
\]

\[
\therefore \quad r_{eff\mid H_2 + CO} \geq r_{eff\mid H_2}
\]

A comparison of the ratios of effective resistance of the circuit, in presence of \( H_2 + CO \) and \( H_2 \) only, for barrier covered Pd films and Pd films without barrier coatings indicates that the increase in effective resistance for the Pd films without the barrier layer is greater than that of films with barrier layer, as shown below.

\[
\frac{r_{eff\mid H_2 + CO}}{r_{eff\mid H_2}} \left\mid_{SiO_2,Pd} \right. = \frac{1 + \frac{r_{CO}}{r_{side,H_2}}}{\frac{1}{r_{CO}} + \frac{1}{r_{H_2} + r_{SiO_2} + r_{side,H_2}}} \]

\[
\frac{r_{eff\mid H_2 + CO}}{r_{eff\mid H_2}} \left\mid_{Pd} \right. = 1 + \frac{r_{CO}}{r_{H_2}}
\]

\[
\frac{1 + \frac{r_{CO}}{r_{side,H_2}}}{1 + \frac{r_{CO}}{r_{H_2} + r_{SiO_2} + r_{side,H_2}}} \leq 1 + \frac{r_{CO}}{r_{H_2}}
\]

\[
\therefore \quad \frac{r_{eff\mid H_2 + CO}}{r_{eff\mid H_2}} \left\mid_{SiO_2,Pd} \right. \leq \frac{r_{eff\mid H_2 + CO}}{r_{eff\mid H_2}} \left\mid_{Pd} \right.
\]

This suggests that the increase in "rc" value for uncoated Pd films due to the presence of CO is larger when compared to Pd films with a barrier layer. Hence, the barrier layer reduces the effect of CO on Pd film response to \( H_2 \).

### 5.7 Sensor Response – Pd/Ni Alloy Thin Films

Palladium hydrogen system is a two phase system (see phase diagram in chapter 2, Figure 2.3). The phase at low concentrations of hydrogen (less than 10 at.% H in Pd, at around 300 K) is known as the \( \alpha \) phase. The second phase with higher concentrations of H in Pd is
known as the $\beta$ phase. $\beta$ phase has a larger lattice volume, hence the phase transformation from $\alpha$ to $\beta$ is accompanied by mechanical instability of the film resulting in blistering or pleeling of the film and an associated change in the resistivity of the metal film. Extending the $\alpha$ phase of Pd-H system was made possible by alloying Pd with another metal that inhibited the dissolution of H$_2$ in Pd. Alloying Pd films with Ni reduces the adsorption and solubility of hydrogen. The reduced adsorption of H$_2$ is thought to occur due to strong interaction of the d-states of Pd and Ni atoms, which in turn reduces the interaction of $\sigma$-states in H atom and d-states in Pd $[2,6]$. In addition, Ni being a smaller atom, shrinks the lattice. The shrinkage counteracts the expansion of the lattice during the adsorption and dissolution of H$_2$ in Pd. This would allow the alloy film to adsorb larger quantities of H$_2$ without increasing the lattice volume (compared to lattice volume of Pd) that would result in phase change ($\alpha$ to $\beta$, see Figure 2.3). It has been established that Pd/Ni alloy thin films with Ni content in excess of (8 to 10%) can extend the $\alpha$ phase all the way to 100 atomic% H in Pd ($\text{H}_{\text{Me}}$/Pd) $[1,16,25]$. However, addition of Ni in Pd lattice, substantially reduces the sensitivity of the alloy film to H$_2$.

5.7.1 Sensor Response – Effect of Hydrogen

Pd/Ni alloy thin film sensors with nickel content of $\sim$7% and $\sim$10% were tested. The sensors had a slower response and lower sensitivity to H$_2$ as seen in Figure 5.33 when compared to sensors with Pd films. Morphologically, Pd/Ni (10%) films have a smoother

![Figure 5.33: Sensor (Pd, Pd Ni films 1000 Å thick, $\sim$1200 Ω) response to 1% H$_2$ in Ar at 100 torr pressure and 75°C sensor temperature.](image)

and denser structure when compared to Pd films (see Figures 4.28, 4.2) deposited under
The smooth morphology would reduce the surface area and limit the number of sites available for adsorption. This could possibly explain the sluggish response of these films when compared to Pd films.

5.7.2 Sensor Response – Effect of Hydrogen and CO

In presence of CO, Pd/Ni alloy films reached their peak values in a shorter time span than Pd films, suggesting diminished effect of CO in these films (see Figure 5.34). However, the rate of adsorption seems to be identical for both these films in the initial period, as seen by nearly identical slopes in the sensor response curves (Figure 5.34). Hence, CO seems to have similar effect (as in Pd films) in slowing down the response of the sensor. However, the rate of desorption of H\textsubscript{2} seems to decrease as the Ni content increases as seen in the shallower slopes during the desorption process (after H\textsubscript{2} flow is turned off).

Figure 5.34: Sensor (Pd, Pd/Ni films 1000 Å thick, ∼1200 Ω) response to 5% CO and 1% H\textsubscript{2} in Ar at 100 torr pressure and 75°C sensor temperature.

5.8 Summary and Discussion

The resistor geometry (area to perimeter ratio, active to non-active area ratio, line width, film thickness, etc.) had little effect on the sensor response to H\textsubscript{2}. This reinforces the fact that the change in resistance of the Pd films in presence of H\textsubscript{2} is a bulk effect. For the change in resistance to occur, it is important that an un-impeded pathway exist for
adsorption, dissociation and diffusion of H into Pd. The fraction of available surface sites for H\(_2\) adsorption is the critical issue and not the total number of sites. Hence, adsorption of CO on Pd surface affects the sensor response, as it reduces the fraction of surface sites available for H\(_2\) to adsorb on. This is responsible for the slowing of the sensor response and a lack of attenuation in sensor sensitivity. This behavior is seen in the Pd thin film sensors measured in this work. Increase in substrate temperature reduces the sensitivity of these sensors due to a lowering of the sticking coefficient of H\(_2\) on Pd. These films conform to Seivert’s law for dissociative adsorption of H\(_2\) in Pd (dR/R = \(\sqrt{P_{H_2}}\)) at low gas pressure.

Thin film morphology was found to have a strong effect on the response of Pd and Pd/Ni alloy thin film chemiresistors to H\(_2\). Effect of morphology on response of Pd/Ni thin films chemiresistors (deposited by co-evaporation) was alluded to by Hughes et al. They performed different anneal treatments in forming gas (4% H\(_2\) in Ar) at temperatures ranging from ~300 to ~550°C on their thin films and concluded that thin films annealed at temperatures in excess of ~300°C showed improved drift free performance to H\(_2\). The improved performance was attributed to finer grain size (measured by AFM). However, the effect of annealing at temperatures ≤550°C should have minimal effect on altering the morphology of the thin films as it is well below the melting point of Pd (~1800°C). It is more likely that the anneals passivated the defects in the thin films, improving the performance and stability of the chemiresistors. By employing magnetron sputtering to deposit Pd and Pd/Ni alloy thin films, it was possible to produce thin films with different morphologies by varying the deposition conditions. At higher deposition pressures Pd films with large columnar grains and rough surfaces were obtained. These films had rough texture and prominent grain boundaries. Conventional wisdom would suggest that this film, having a larger surface area, would be more sensitive and respond faster to H\(_2\). However, the presence of grain boundaries provides an additional pathway for H\(_2\) adsorption, that is diffusion limited and hence slows the sensor response. The higher resistivity of this thin film due to the presence of grain boundaries reduces the overall sensitivity to H\(_2\). A simple circuit model consisting of resistors and capacitors was used to illustrate the mechanism of H\(_2\) transport to the Pd surface and its subsequent diffusion into the bulk in thin films with different morphologies.

SiO\(_2\) thin films on the top surface of Pd thin film resistors improved the sensor response significantly in presence of CO and H\(_2\) in Ar. This improvement in performance was attributed to the blocking of CO from reaching the Pd surface and selective diffusion of H\(_2\) through SiO\(_2\). The role of the side walls of the metal lines (not covered by SiO\(_2\)) were also found to be important in explaining the response of these sensors. The side wall provides an alternate path for H\(_2\) to diffuse into Pd and a potential surface for CO to physisorb. Solubility of H\(_2\) in SiO\(_2\) and the trapping of some dissolved H\(_2\) in Pd was thought to be responsible
for the increased sensitivity and drift in response of these chemiresistors. A simple circuit model consisting of resistor and capacitor (representing the solubility of H$_2$ in H$_2$ and SiO$_2$) elements was used to explain the increased sensitivity and improved chemiresistor response in presence of CO and H$_2$.

Alloying Pd with Ni reduced the sensitivity of the thin film to H$_2$. This is attributed to the shrinking of the alloy lattice [4], preventing H atoms from occupying the octahedral interstitial sites. These alloy films can detect larger concentrations of H$_2$ without undergoing the $\alpha \rightarrow \beta$ phase transition. Work done by Hughes et al [1, 16, 25] indicates that Pd/Ni alloys with Ni content in the range of 8 to 20 atomic % do not show any phase change for H$_2$ concentrations in the range of 0 to 100%. However, as indicated before, this gain comes at the cost of reduced sensitivity to H$_2$. Addition of Ni does little to counter the effect of CO in slowing down the response of these chemiresistors to H$_2$. 
References


Chapter 6

Conclusions and Future Work

Pd has long been known to adsorb hydrogen and modify its electrical and physical properties. Sensors utilizing these property changes have been tested and found to work effectively over a wide range of hydrogen concentrations. However, in the presence of gases such as CO, H$_2$S, SO$_2$ and O$_2$, these sensors are constrained in their response to H$_2$. Improving the performance of Pd based chemiresistor sensors for detection of hydrogen gas in harsh environment (high pressure, gas mixtures and high flow rates) have been explored through varying resistor geometry, thin film morphology and incorporation of semi-permeable barrier layers.

6.1 Conclusion

The sensors were fabricated with sputter deposited Pd and Pd/Ni alloys. By sputtering, it was possible to control the film morphology and alloy composition. To obtain a better understanding of the Pd and Pd/Ni thin film morphology, ion energy distribution of the plasma was characterized. Measurements were made on sensor structures to study the effect of sensor geometry, temperature, partial pressure of gas, different gas compositions, thin film morphology, Pd/Ni alloy compositions and semi-permeable barrier layers. The important results are summarized below.
6.1.1 Morphology and IEDF Studies

- Increasing the deposition gas pressure from 5 to 25 mtorr had a profound effect on the DC sputtered Pd thin film morphology. SEM micrographs of films deposited at higher gas pressures had a rougher texture with distinct grain boundaries. This morphology was attributed to changes in the energy of the neutrals bombarding the substrate. Little change was measured in the ion energy distribution function of Pd and Ar ions (process gas).

- IEDF measurements with pulsed DC source indicate that a significant flux of energetic ions (∼ 65 eV) bombard the substrate. This results in a film with denser morphology and greater amount of oriented facets (for deposition with targets at 45° off the normal to the substrate). The energetic ions are attributed to changes in the plasma during the pulsing cycle.

- In pulsed DC plasma, the ion energy distribution function was dependent on the input pulse shape of the power source and the geometry of the deposition system. Changes in pulse width (time corresponding to the flat portion of the positive cycle in the input pulse signal), frequency, power and pressure had little effect on the shape of IEDF.

- Co-sputtering Pd and Ni to deposit alloy films leads to smooth and dense columnar films. When compared to to Pd films the alloy films are smoother and the columns are more closely packed. This is due to the contraction of Pd lattice on addition of Ni (smaller atomic radii).

6.1.2 Sensor Characterization

- Based on resistance measurements on structures with different geometries, it was found that there was no discernible change in resistance due to resistor geometry.

- Higher temperatures reduced sensor sensitivity to hydrogen in accordance with lower sticking coefficients of H₂ molecules on Pd. The sensor response (dR/R) data at different temperatures was in good agreement with Clausius Clayperon equation. However the signal to noise ratio was reduced resulting in increased jitter in sensor signal. A significant drift in sensor response was observed.

- The sensors obeyed Seivert’s law (dR/R ∝ \( \sqrt{P_{\text{H}_2}} \)) for a wide range of H₂ concentration at pressure below atmospheric pressure. This is in accordance with the kinetics of dissociative adsorption of diatomic gas molecules on metal surfaces.
• SO$_2$ irreversibly poisoned the sensor by depositing sulfur on the Pd surface and attenuating its response.

• CO slows down the sensor response significantly, but does not attenuate the response. This effect was reversible. At higher temperature the effect of CO was significantly reduced due to lowering of its sticking coefficient on Pd.

• Pd films with a rough texture and prominent grain boundaries were less sensitive to H$_2$ and CO. The insensitivity to CO is thought to be due to This response is explained using a simple circuit model based on series and parallel resistors.

• SiO$_2$ films (up to 800Å thick) improved sensor response when exposed to gas mixtures containing CO and H$_2$. However drift was an issue of concern. Also, the oxide only covered the top surface of the metal line and left the side walls open. The exposed side walls is thought to be responsible for some of anomalous behavior of these sensors. The response of these sensors is explained using parallel capacitor-resistor circuits. The capacitor represents the solubility of H$_2$ in SiO$_2$. The dissolved H$_2$ is important during the adsorption/desorption process and introducing a capacitor in the circuit brings about a time dependence in response of the circuit during power-up or shutdown phase.

• Pd/Ni alloy films had lower sensitivity to H$_2$ as Ni content was increased (up to ~25% Ni and insensitive beyond that at low temperatures <200°C). The response rate was also marginally slower than Pd films.

6.2 Future Work

Improvements in sensor performance would depend on improving the fabrication process, optimizing the morphology and barrier layers.

6.2.1 Sensor Fabrication

The sensor structures tested thus far had critical yield and uniformity issues, mostly associated with the lift-off technique (chlorobenzene soak) and the handling of the wafers during processing. The sputter system was capable of handling samples of 1×1 inch$^2$ size only, hence the wafer had to be cleaved into this size after the second lithography step. This is thought to cause defects in the pattern, leading to yield and uniformity issues. The
problem can be overcome by processing complete wafers using improved “lift-off” methods using dual resist layers.

6.2.2 Barrier Layers

SiO$_2$ showed promise in mitigating the effect of CO on the sensor performance. However, due to the current fabrication method, the side walls of the metal lines were not covered by the oxide. This possibly could be responsible for the observed response of these sensors to H$_2$ and CO. Sensor structures with complete barrier layers need to be tested. This requires additional processing steps.

In addition to SiO$_2$, silicon oxycarbides and oxynitrides are also potential candidates for barrier layers. Sensors with these materials as barrier layers need to be tested to determine their effectiveness. Also, some of these materials may be more effective against other gases that affect the sensor response.

6.2.3 Thin Film Morphology

Measurements on sensors with different thin film morphology indicate that significant differences in sensor performance. However, further investigation needs to be made on a wider range of morphologies to completely understand the effect of morphology.

6.2.4 Plasma Characterization of Sputter Discharge

IEDF of pulsed DC sputter discharge (used to deposit SiO$_2$ and Ni) indicates a high energy peak associated with the pulsing of the plasma. Langmuir probe measurements would be helpful in correlating the ion flux with the pulsing, to establish the origin of the high energy peak. Also, measuring the energy distribution of neutrals at the substrate would help in understanding the morphology of the films. Optical emission spectroscopy would help in following the relative flux of Argon ions (Ar$^+$ and Ar$^{++}$) and could shed light on changes in the plasma in pulsed DC discharges when compared to DC sputtering discharges.
6.2.5 Differences in Adsorption/Desorption Mechanisms

Response of chemiresistors to H\textsubscript{2} and CO is different from that of capacitors. In capacitors CO causes an attenuation in the sensor response. However, in chemiresistors, CO slows down the sensor response but does not cause attenuation in sensor signal. Data in literature for capacitors have gate thin film deposited by evaporation which results from a very different morphology when compared to sputter deposited films. Measuring response to H\textsubscript{2} and CO on films with identical morphology, as in chemiresistors will help in resolving this issue.

6.2.6 Pd/Ni alloys

Pd/Ni alloy films with up to 25\% Ni have been shown to prevent phase transformation in PdH. However, this gain is achieved by loosing sensitivity to H\textsubscript{2}. Also, alloys with higher Ni content may be useful for sensing H\textsubscript{2} in high pressure environments (> 1 atm).

6.2.7 Other Pd alloys

Numerous alloys of Pd, Pd/Ni, Pd/Ag, Pd/Cu, Pd/Cr, Pd/B, Pd/Au, have been studied for their response to H\textsubscript{2}. As a rule, larger substitutional atoms like Au, cause expansion of the Pd lattice, leading to increased solubility of H\textsubscript{2} and hence \(\alpha\) to \(\beta\) transformation at lower H\textsubscript{2} concentrations. Lattice expansion would also occur when the atoms occupy interstitial site as is the case with B. On the other hand smaller atoms occupying substitutional site, like Ni would lead to contraction of the lattice site reducing the solubility of H\textsubscript{2} in the alloy, thus extending the \(\alpha\) phase. However, many of these alloy have multiple phases, increasing the probability of phase transformation. This is not desirable for sensor applications.
Appendix A

Sensor Testing Circuit

Figure A.1: Chemiresistor measurement circuit.
Appendix B

Sensor Die Design

Figure B.1: Mask layout of the chemiresistor showing the four parts of the die.
Figure B.2: Layout of 4000µm long and 10µm wide line and line with same length to width ratio, but different geometries.
Figure B.3: Layout of 8000\(\mu\)m long and 10\(\mu\)m wide line and line with same length to width ratio, but different geometries.
Figure B.4: Layout of 14000µm long and 20µm wide line and line with same length to width ratio, but different geometries.
Figure B.5: Layout of 2000µm long and 10µm wide line and lines with length to width ratio of 700 but different geometries.
Appendix C

Diffusivities of H$_2$ and O$_2$ in SiO$_2$

Figure C.1: Diffusivities of Hydrogen and Oxygen in thermally grown SiO$_2$ as a function of temperature [1]
C.1 Calculated Mean Free Diffusion Times Through SiO$_2$

The mean free distance covered by a molecule by diffusion is given by $\sqrt{2Dt}$. Hence the ratio of times taken by O$_2$ and H$_2$ molecule to diffuse through SiO$_2$ would be given by ratio of the diffusivities of H$_2$ and O$_2$ [2].

$$\frac{t_{O_2}}{t_{H_2}} = \frac{D_{O_2}}{D_{H_2}}$$

At $\sim 75^\circ C$, $D_{O_2} \approx 10^{-22}cm^2/s$ and $D_{H_2} \approx 10^{-10}cm^2/s$. Hence the ratio of the mean diffusion time is

$$\frac{t_{O_2}}{t_{H_2}} = \frac{10^{-10}}{10^{-22}} = 10^{12}$$

From the calculation it is clear that SiO$_2$ is an efficient barrier for separating O$_2$ molecules from H$_2$. 


References


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